Supporting Information: Hydrogen Bonding Constrains Free Radical Reaction Dynamics at Serine and Threonine Residues in Peptides

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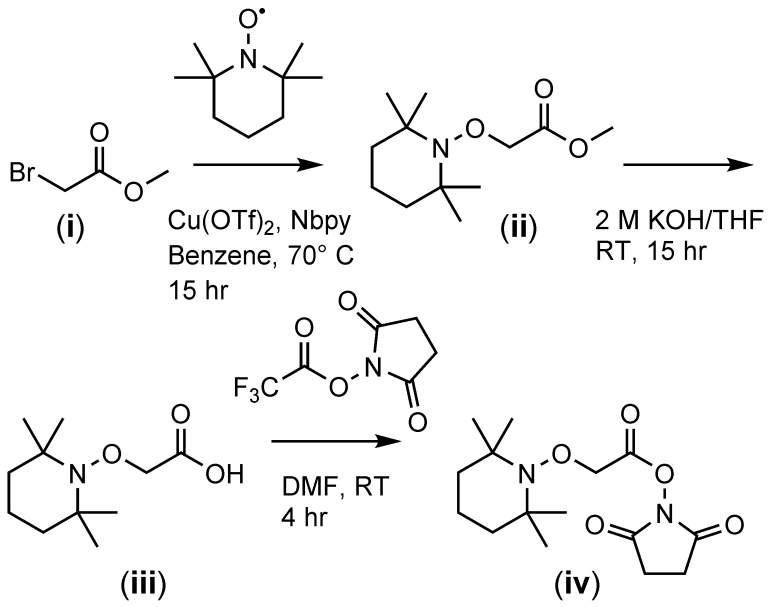
Synthesis of TEMPO-based FRIPS reagent.

Scheme S1. Synthesis method for FRIPS reagent



The synthesis strategy for the second generation TEMPO-based FRIPS reagent (10) is summarized in Scheme S1. The previous development by Lee et al.[1] was modified by replacing 2-(bromomethyl)benzoic acid methyl ester with methyl 2-bromoacetate for the current study, as outlined briefly previously.[2] Further details are given here.

Methyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetate (ii)

A 25 mL, 3-neck flask equipped with a teflon-coated, oval shaped magnetic bar was flame-baked under vacuum, charged with dry N_2 gas, and cooled down to room temperature. To the flask was added methyl 2-bromoacetate (i) (0.474 mL, 5 mmol, 1 equiv), TEMPO (957 mg, 6 mmol, 1.2 equiv), $Cu(OTf)_2$ (185 mg, 0.5 mmol, 0.1 equiv), copper powder (318mg, 5 mmol, 1 equiv), 4,4′-dinonyl-2,2′-bipyridyl (Nbpy, 843 mg, 0.4 equiv), and benzene (10 mL, 0.5 M). The reaction mixture was degassed by bubbling dry N_2 gas and stirred at 70 °C for 15 h under a stream of dry N_2 gas while monitoring conversion by thin layer chromatography (hexane : ethyl

acetate = 10 : 1, $KMnO_4$). The crude mixture was cooled down to room temperature, briefly cleaned by filtration through a short pad of silica gel, and the silica gel pad was thoroughly washed by ethyl acetate (EtOAc) to recover the product. The filtrate was washed by saturated NH_4Cl, and 1 M NH_4OH to remove the residual copper ions. The organic layer was further washed by saturated brine, dried over anhydrous $MgSO_4$, concentrated by a rotavap, and purified by silica gel column chromatography (hexane : EtOAc = 20 : 1). The desired product, methyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetate (ii) (1.023g, 4.46 mmol) was obtained as a yellow oil. Yield: 89%. R_f = 0.44 (hexane : EtOAc = 10 : 1); electrospray ionization (ESI)-MS $[M+H]^+$ = 230.1 m/z; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.45 (s, 2H), 3.74 (s, 3H), 1.54 (br, 1H), 1.45 (br, 4H), 1.32 (br, 1H), 1.15 (s, 12H); ^{13}C NMR (125 MHz, CDCl3): δ 170.22, 75.37, 60.06, 51.55, 39.68, 32.71, 20.07, 17.01.

2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetic acid (iii)

To a 25 mL, one-neck flask was added methyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetate (**ii**) (246 mg, 1.07 mmol, 1 equiv), tetrahydrofuran (THF) (5 mL), and 2 M Potassium Hydroxide (KOH, 5 mL). The mixture was stirred at room temperature for 24 h. The reaction was monitored by thin layer chromatography and ESI-MS until the starting material was completely consumed. Upon completion of the reaction, THF was removed by rotavap, and the residual aqueous layer was neutralized by ~5 mL of 2 M HCl to yield a pH of ~6. The mixture was extracted by CH_2Cl_2 (×5), and the combined organic layer was dried over anhydrous $MgSO_4$, concentrated by rotavap, and purified by silica gel column chromatography (hexane : EtOAc = 2 : 1) to yield 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetic acid (**iii**) (137 mg, 0.635 mmol) as a white powder. Yield: 59%. R_f = 0.2 (hexane : EtOAc = 1 : 1); ESI-MS $[M+H]^+$ = 216.1 m/z; ^{1}H NMR (500 MHz,

$CDCl_3$): δ 12.6 (br s, 1H), 4.29 (s, 2H), 1.50-1.23 (br m, 6H), 1.08 (d, *J* = 14.4 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.10, 75.53, 59.86, 39.59, 32.82, 20.31, 16.99.

2,5-dioxopyrrolidin-1-yl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetate (iv)

In a flame-baked 50 mL one neck flask, *N*-hydroxysuccinimide (2.75 g) was added to 14 mL of trifluoroacetic anhydride at room temperature under a stream of dry N_2 gas and stirred for 4 h. The solvent was removed by rotavap and further eliminated by high vacuum overnight. The white crystal product, trifluoroacetic *N*-hydroxysuccinimide ester (TFA-NHS) was obtained, stored in a desiccator, and used just before activation of free acids.

To a flame-baked, 15 mL, one-neck flask was added 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetic acid (**iii**) (61 mg, 0.283 mmol, 1 equiv), TFA-NHS (270 mg, 1.28 mmol, 4.5 equiv), and dry DMF (1 mL). The mixture was stirred for 24 h and purified by flash column chromatography (hexane: EtOAc = 3 : 1 ~ 1 : 1), yielding the desired product, 2,5-dioxopyrrolidin-1-yl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)acetate (**iv**) (83.5 mg, 0.267 mmol). Yield: 95%. ESI-MS (100% acetonitrile (ACN) for solvent) $[M+H]^+$ = 313.1 m/z. The stock solution of the TEMPO-based FRIPS reagent (**iv**) was prepared without further analysis at the concentration of 10 mg/mL in ACN, and stored in -20 °C in separate vials. Each stock vial was used for conjugation with peptides as needed.

Chemistry of the FRIPS reagent.

As discussed in the main text, the singly-protonated peptide derivatized with the TEMPO-based reagent was isolated and subjected to CID, producing the acetyl radical peptide ion (right hand side of Scheme 1). Further dissociation of this species by collisional activation produced the desired FRIPS spectrum. Higher charge states were not examined because the relatively high proton affinity of the TEMPO residue can lead to protonation of the FRIPS reagent, resulting in rearrangement to give a neutral loss of $C_9H_{19}N$ (−141 Da) that competes with free radical generation.

This work utilizes model peptides to investigate the dissociation pathways of the acetyl radical generated by FRIPS. Taking advantage of the selective nature of hydrogen-deficient free radical peptide chemistry, alanine residues, which are largely unreactive due to their high C_β−H BDE (~100 kcal/mol),[3-4] are utilized as "spacers" in a peptide of the form AARAAAXAA or AARAAXAYA, where the arginine residue provides a protonation site, and X and Y represent the amino acids of interest. Reaction of the radical center with arginine to yield side chain loss or backbone cleavage is minor compared to reaction with the amino acids more distant from the N-terminus denoted X and Y, as evidenced by minimal product ion formation from dissociation at arginine residues in these experiments. This approach allows for targeted study of the chemistry of any single residue or the comparative reactivity of a pair of residues.

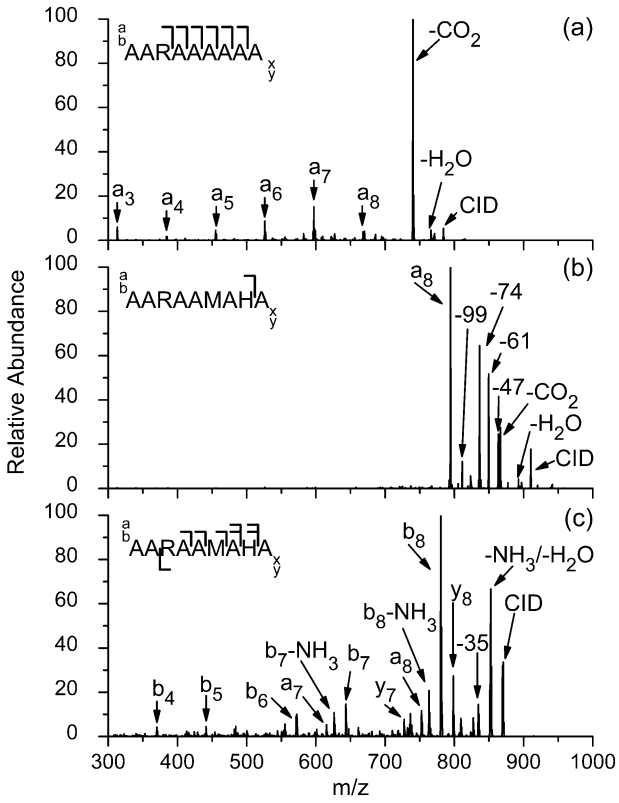


Figure S1. Characteristic FRIPS product ions observed in model peptides; (a) the FRIPS spectrum of AARAAAAAA is dominated by neutral loss of CO_2 and also displays a series of a ions with a_7 the most abundant; (b) the FRIPS spectrum of AARAAMAHA illustrates the typical FRIPS product ions, with backbone cleavage occurring at the histidine residue to yield the a_8 ion and side-chain losses occurring from methionine (−74, −61, −47) and arginine (−99) residues. FRIPS (b) shows greater selectivity in dissociation than CID (c).

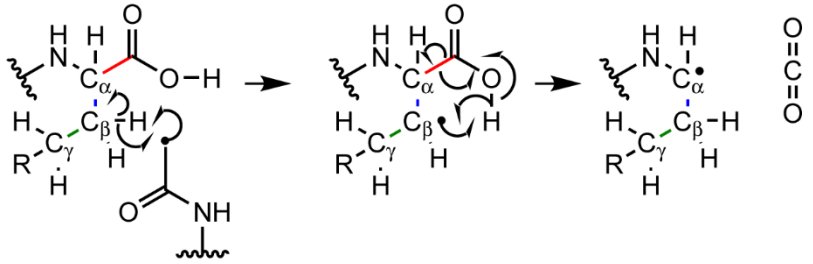
The spectra shown in Figure S1 demonstrate the free radical chemistry of three model peptides of the type employed in this work. Figure S1a shows the FRIPS spectrum of AARAAAAAA, which shows only loss of CO_2 as a major product ion, with minor abundance of a ions (a_3-a_8) formed at alanine residues along the backbone. The predominance of CO_2 loss in spite of the high BDE of the carboxylic acid O−H bond (~112 kcal/mol) suggests that this process may occur

via hydrogen atom transfer to a radical center at C_β of the C-terminal residue in concert with β-cleavage of the C_α–C bond (Scheme S2).[4-5] Also of note, a_n ion formation occurs most prominently at the 7th residue of the peptide and decreases in abundance approaching the N-terminus, demonstrating the somewhat regioselective reactivity of the acetyl radical in these model peptides. This selectivity is hypothesized to result from the tendency of the acetyl radical on the N-terminus to be in close proximity to these residues in the gas-phase low-energy structures of the protonated peptides, which can increase reactivity at these sites. It is likely that such proximity results from the formation of multiple electrostatic interactions between the peptide backbone and the site of protonation at arginine to yield a globular peptide structure, a common effect observed in gas-phase protonated peptide structures.[6-7] The present study derives advantage from this observation, informing a choice of model peptides to optimize reaction around the seventh residue.

In contrast to the FRIPS products of the alanine model peptide, the FRIPS spectrum of AARAAMAHA in Figure S1b shows little CO_2 loss or backbone a ion formation at alanine residues and is instead dominated by dissociation at methionine and histidine. The formation of the a_8 ion through hydrogen atom abstraction at C_β followed by β-cleavage of the backbone C_α–C bond suggests a low activation energy for these processes at the histidine residue. In contrast, hydrogen abstraction at the methionine residue occurs from C_γ, C_α, and C_β, resulting in neutral losses of CH_3SCHCH_2 (−74 Da), $CH_3SCH_2^\bullet$ (−61 Da), and $CH_3S^\bullet$ (−47 Da), respectively, through β-cleavage processes that are more favorable than backbone dissociation at this moiety.[3] Taken as a whole, these FRIPS spectra demonstrate that the current generation FRIPS reagent displays similar dissociation pathways to those observed for both the previous generation reagent and for other hydrogen-deficient radical dissociation methods.[3, 8-9] Compared to CID of the

underivatized peptide (Figure S1c), FRIPS exhibits greater selectivity in its cleavage sites, giving extensive reaction only at certain side chains, which is attributed to the relatively high activation energies for C_β–H abstraction and/or β-cleavage at alanine.[3] Although FRIPS may not produce sequence coverage from residues of low reactivity, its specificity can yield sequence information complementary to conventional CID, where highly selective cleavage processes frequently occur (e.g. at aspartic acid residues),[10-13] making it useful for peptide sequencing applications.[2]

Scheme S2. Possible Mechanism for Loss of CO_2 from Peptides in FRIPS Spectra

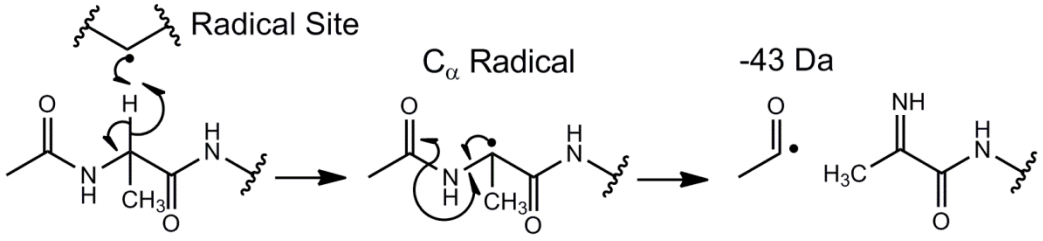


Analysis of FRIPS Product Ions in Serine/Threonine Peptides by MS^n

To further characterize the product ions observed in the FRIPS spectra of serine and threonine model peptides, MS/MS experiments were performed on the prominent ions in each spectrum. Figure S2a shows the CID spectrum of the a_7 ion produced by FRIPS of the model threonine peptide, and the identified product ions support the process shown in Scheme 2b, with product ion formation occurring via β-cleavage of the C_α–C bond. The c_6 ion was also subjected to CID as shown in Figure S2b, and all identified product ions also agree with the standard c ion structure formed by cleavage of the N–C_α bond. Information about the structure around the site of backbone cleavage is limited, as only one C-terminal ion was observed, but the prevalence of b- and y-type ions does indicate that this product ion constitutes an even-electron species. In contrast, the CID spectrum of the $[a_6+H]^\bullet$ ion shown in Figure S2c contains much more

prominent a-type ions in addition to internal fragment ions, supporting the assertion that this product represents a radical species. This radical likely dissociates through further hydrogen abstraction events to give the observed a-type ions, whereas the internal fragments may be formed by combined b- and y-type or a- and y-type ion formation. A prominent neutral loss of 43 Da was also observed and was attributed to the loss of $CH_3C(O)^{\bullet}$ from the N-terminus via β-cleavage of the peptide bond between the acetyl group and the first alanine residue following hydrogen abstraction from C_α of alanine, as shown in Scheme S3. The odd-electron nature of the proposed $[a_6+H]^{\bullet}$ ion is further supported by the interaction of the ion with oxygen gas in the trap to give the peroxy radical species denoted in Figure S2c as $[M+H+O_2]^{+\bullet}$, which forms by oxygen attachment at the radical site. Such behavior has been previously characterized for radical z ions produced by ECD as well as in hydrogen-deficient radicals formed by photodissociation.[14-15] Similar experiments were performed on the major product ions observed by FRIPS of AARAAASAA, and the $[a_6+H]^{\bullet}$, c_6, and a_7 ions gave spectra nearly identical to those obtained for AARAAATAA. Collisional activation of the neutral loss of CO_2 resulted in a spectrum similar to the initial FRIPS spectrum, indicating that further hydrogen-deficient radical chemistry dominated in the dissociation of this ion (data not shown).

Scheme S3. Proposed Mechanism for Loss of $CH_3C(O)^{\bullet}$ (-43 Da)



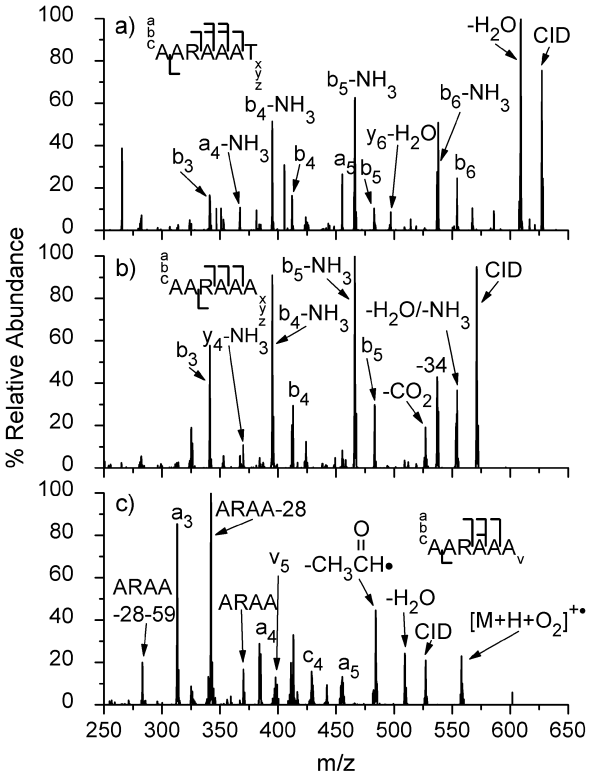


Figure S2. MS/MS analysis of product ions in the FRIPS spectrum of AARAAATAA. The a_7 ion (a) shows product ions consistent with proposed structure shown in Scheme 2b. Similarly, CID of the c_6 ion (b) yields product ions that agree with a structure similar to that observed in ECD spectra. The radical nature of the $[a_6+H]^{\bullet}$ ion is supported by the abundance of a-type ions and internal fragments in the CID spectrum shown in (c), as well as the by the formation of the peroxy radical species.

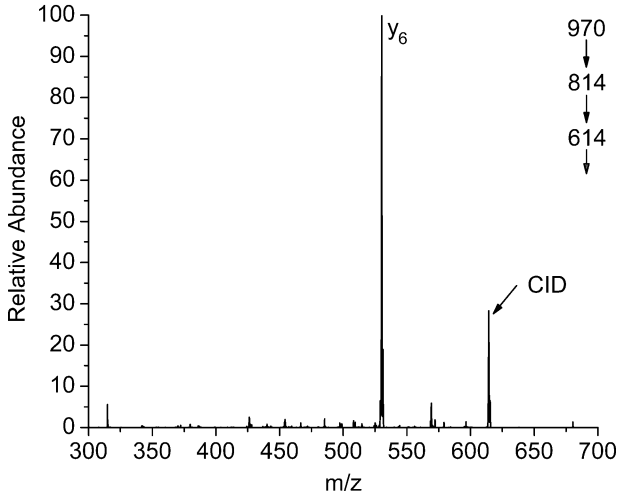


Figure S3. MS^4 spectrum of z_7 ion produced by FRIPS of the model peptide AATAAARAA.

Additional Computational Chemistry

Calculated Energetics for Hydrogen Atom Abstraction. To assess the likely rate-limiting step in free-radical initiated dissociation at serine and threonine residues, the energetics for hydrogen abstraction from C_α and C_β of the threonine model compound were calculated using *N*-methylacetamide as the N-terminal acetyl radical analog, as shown in Figure S4. Beginning from the low-energy structure found for the threonine model compound (**S1**), the energetics of approach of the *N*-methylacetamide radical from a variety of initial approach trajectories was calculated, and the lowest activation energy found is reported here. Product ion structures are those found from IRC calculations and match conformations found previously for the C_α and C_β-centered radicals (Figure 3). The activation energy for abstraction from C_α (Figure S4a) was found to be slightly higher (~2 kcal/mol) than that for abstraction from C_β (Figure S4b), although the reaction enthalpy for the two processes was quite similar. Similar barrier heights were found regardless of the density functional utilized, although M05-2X and M06-2X predicted reaction enthalpies higher than those from B3LYP by ~3 kcal/mol.

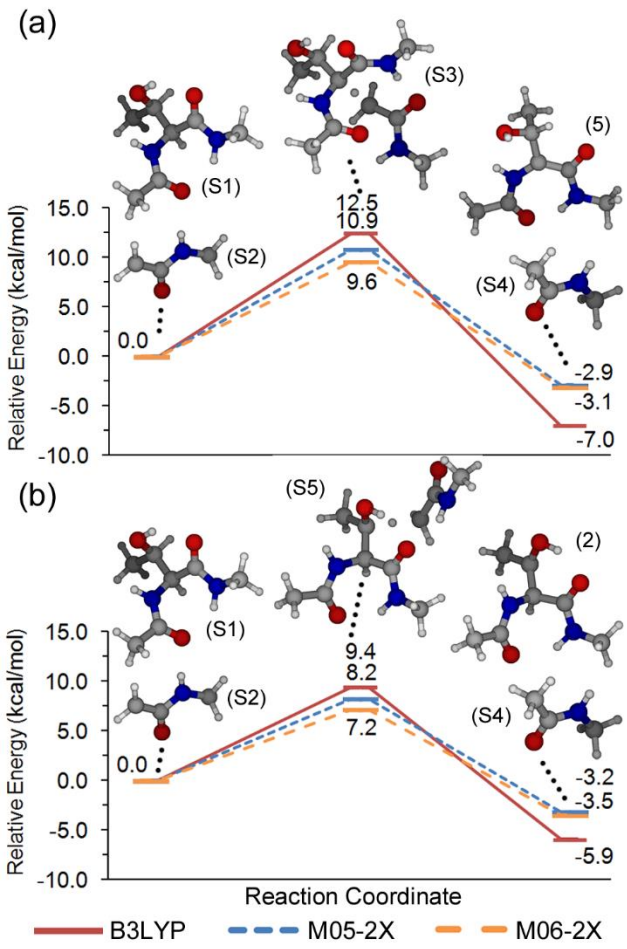


Figure S4. Energetics for hydrogen atom abstraction by *N*-methylacetamide from threonine model compound. Similar reaction enthalpies were calculated for hydrogen abstraction from C_α (a) and C_β (b), although the activation energy was slightly higher for abstraction from C_α.

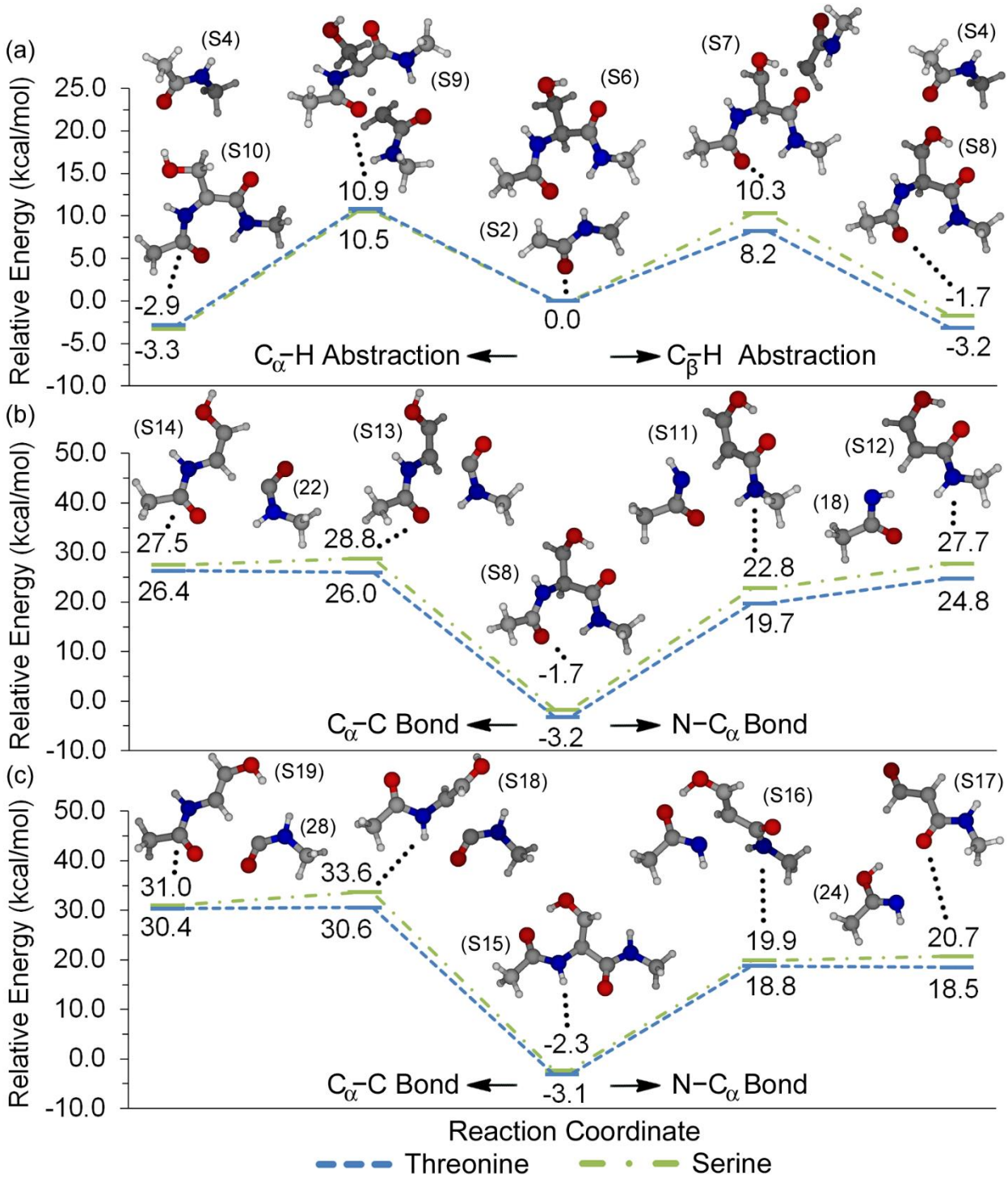


Figure S5. Energetics for serine model system versus threonine model system. For clarity, only M05-2X energetics are shown, with energetics referenced to the ground state conformation of the even-electron species and the *N*-methylacetamide radical. Structures shown are those for the serine model system. Shown in (a) are the energetics of C_α–H and C_β–H abstraction, whereas (b) and (c) show energetics for C_α–C and N–C_α bond cleavage from the C_β-centered radical with C-terminal and N-terminal hydrogen bonding structures, respectively.

Table S1. Energetics of Serine Model Compound Shown in Figure S4 with Three DFT Methods.

	ΔH (298 K, ZPE Correction)		
Reaction	B3LYP	M05-2X	M06-2X
S2+ S6 → S7	11.2	10.3	9.3
S2 + S6 → S4 + S8	-3.6	-1.7	-1.9
S2+ S6 → S10	12.1	10.5	9.5
S2 + S6 → S4 + S11	-7.4	-3.3	-3.5
S8 → S12	17.3	24.5	23.8
S8 → S13 + 18	18.0	29.4	29.5
S8 → S14	24.5	30.5	29.7
S8 → S15 + 22	18.8	29.2	27.6
S2 + S6 → S4 + S16	-4.0	-2.3	-2.7
S16 → S17	17.0	22.2	23.0
S16 → S18 + 24	13.2	23.0	22.6
S16 → S19	29.7	35.9	35.3
S16 → S20 + 28	22.6	33.3	32.1

***O*-methylthreonine Reaction Energetics.** The reaction energetics of the *O*-methylthreonine model compound 2-acetamido-3-methoxy-*N*-methylbutanamide were also investigated. As with the valine molecule, only the lowest energy conformer of the β-carbon radical species was examined. This conformer (6), as shown in Figure S6a, displays an all-trans backbone, with hydrogen bonding between the N-terminal backbone amine and the methylated oxygen of the threonine side chain.

In contrast to the hydrogen bonding structures of the threonine model compound, the *O*-methylthreonine N−C_α bond reaction coordinate (Figure S6a) revealed that maintaining hydrogen bonding following dissociation was not energetically favorable due to the optimal position of the methylated side chain away from the backbone as seen in the C-terminal product (**S23**). This process occurs with a barrier of ~30 kcal/mol, with a noncovalent complex formed through interactions between the N-terminal nitrogen and C-terminal carbonyl at 23-31 kcal/mol, and a final enthalpy of reaction of 30-40 kcal/mol, depending on the density functional used. As shown in Figure S6b, the C_α−C bond dissociation required rotation of the side chain at the transition state (**S24**) to enhance π-orbital overlap without significant steric repulsion. The reaction enthalpy was calculated to be 22-31 kcal/mol, with a barrier of 23-29 kcal/mol. The cleavage of the C_α−C bond was therefore found to be more favorable by nearly 8 kcal/mol using B3LYP, and the energetic difference between the pathways is even larger for the M05-2X and M06-2X density functionals.

It was speculated that the loss of isocyanic acid from the N-terminal nitrogen-centered radical may occur as a concerted process with N−C_α bond cleavage for this species, making this pathway more favorable than C_α−C bond dissociation. Although the investigation of the concerted cleavage of the N−C_α and N-terminal C_α−C bonds was not possible due to initial conformational diversity, the energetics of the loss of isocyanic acid from a model alanine compound containing a nitrogen-centered radical were examined. The alanine model compound was chosen for its similarity to the radical likely generated experimentally in the peptides used in this study. The lowest energy conformer (**9**) shown in Figure S6c possesses a backbone in the all-trans configuration, with the alanine side chain positioned off-axis from the peptide chain and the nitrogen radical center in the plane of the backbone.

The calculated reaction coordinate for the loss of isocyanic acid by cleavage of the C_α–C bond is shown in Figure S6c. The reaction has a low barrier of 3.2 kcal/mol, with a reaction enthalpy of -11.3 kcal/mol. The transition state structure (**S27**) contains a hydrogen bond between the nitrogen-centered radical and the carbonyl oxygen that forms as the C_α–C bond elongates. The hydrogen bonding interaction is subsequently broken as the planar isocyanic acid structure (**S29**) is formed along with the carbon-centered radical on the N-terminal product (**S28**). The enthalpy calculations using the B3LYP density functional suggest that this process could cause N–C_α bond dissociation to be favored over cleavage of the C_α–C bond if the reactions occur in a concerted fashion. However, the M05-2X and M06-2X density functional give a higher barrier and less energetically favorable products that do not support this assertion. In addition, it is not clear why such a concerted process would occur in the case of *O*-methylthreonine but not in other amino acid side chains. Thus, dissociation to give the experimentally observed $[a_6+H]^\bullet$ ion likely occurs via loss of methanol from the side chain, followed by β-elimination of the N-terminal C_α–C bond, as discussed in the main text.

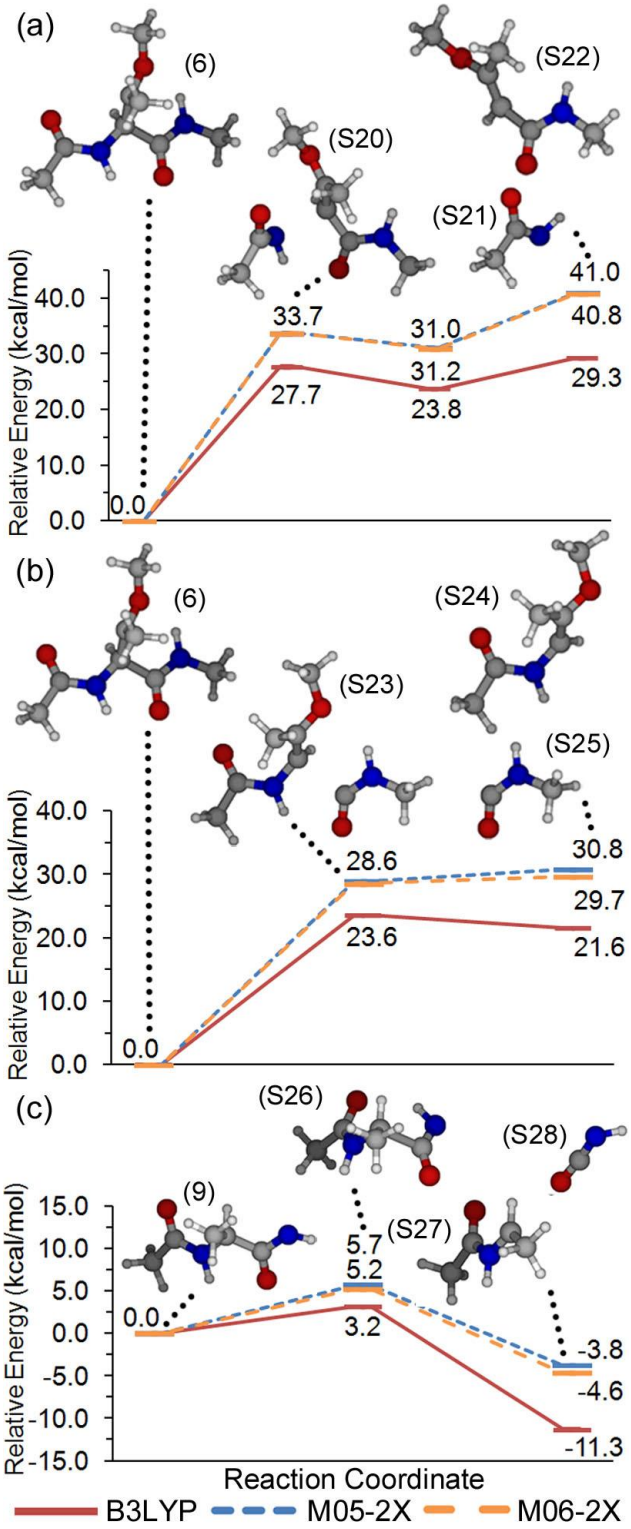


Figure S6. Reaction energetics for the lowest energy conformer of the *O*-methylthreonine model compound; (a) N−C_α reaction coordinate, (b) C_α−C reaction coordinate, (c) energetics of loss of isocyanic acid. C_α−C bond cleavage is enthalpically favored by greater than 8 kcal/mol over N−C_α bond cleavage, suggesting that an alternate mechanism leads to $[a_{n-1}+H]^\bullet$ ion formation.

Table S2. Coordinates, energetics, and partial charges for model valine compound with radical center at C_β, Structure (**1**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	6.404857	1.605255	-0.602635	0.76017	0.25117	0.66944
N2	4.244684	1.296299	-1.613399	-0.35831	-0.26361	-0.63583
C3	5.160482	0.673039	-0.660295	-0.42872	-0.0831	-0.15565
C4	5.50478	-0.762205	-0.979035	0.37289	-0.24916	0.08299
C5	5.033604	-1.858743	-0.078292	-0.357	-0.31845	-0.64651
O6	6.407821	2.712789	-1.124245	-0.54756	-0.40046	-0.63766
N7	7.451801	1.117193	0.100635	-0.48705	-0.36077	-0.61538
C8	2.935481	0.932772	-1.706466	0.80589	0.14457	0.66459
O9	2.472165	-0.022053	-1.096464	-0.5998	-0.37912	-0.64202
C10	2.083647	1.784364	-2.632678	-0.77404	-0.37456	-0.66359
C11	8.692251	1.864189	0.262096	-0.14595	-0.21535	-0.37487
H12	4.565646	2.179545	-1.992591	0.24475	0.29139	0.41819
H13	4.702918	0.703359	0.337244	0.16387	0.2018	0.22817
H14	4.978899	-1.54146	0.967825	0.07329	0.12158	0.20637
H15	4.017741	-2.178255	-0.357659	0.14514	0.186	0.23887
H16	5.683903	-2.738289	-0.140789	0.07666	0.12783	0.20364
H17	7.414791	0.147192	0.376858	0.27923	0.30452	0.39927
H18	1.615732	1.133767	-3.374614	0.20527	0.17587	0.22943
H19	1.28311	2.243549	-2.04764	0.20875	0.17555	0.22964
H20	2.648153	2.566021	-3.144361	0.19489	0.12928	0.20286
H21	9.311713	1.358014	1.002448	0.1122	0.1219	0.1988
H22	8.476467	2.876103	0.608283	0.09625	0.16243	0.21265
H23	9.244472	1.935824	-0.679712	0.09398	0.15208	0.19695
C24	5.937585	-1.101909	-2.370335	-0.61854	-0.34695	-0.65157
H25	6.474099	-0.279859	-2.853389	0.15554	0.15349	0.21183

E[B3LYP/6-311++G(d,p)]:	-573.997695	hartree
E[M05-2X/6-311++G(d,p)]:	-573.907557	hartree
E[M06-2X/6-311++G(d,p)]:	-573.739471	hartree
ZPE[B3LYP/6-311++G(d,p)]:	142.22	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.713	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-573.756	hartree

Table S3. Coordinates, energetics, and partial charges for model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**2**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	5.791831	-0.331752	-1.196678	0.52088	0.31953	0.66876
N2	4.552809	0.835225	0.588231	-0.35105	-0.32081	-0.6229
C3	4.389741	0.031844	-0.653891	-0.22678	-0.23376	-0.18171
C4	3.538169	0.738245	-1.665765	0.15575	-0.11854	0.32038
C5	2.070601	0.889454	-1.456443	-0.35785	-0.34535	-0.64939
O6	4.115275	1.738368	-2.39266	-0.46569	-0.23764	-0.71061
O7	6.32148	0.302413	-2.11366	-0.48832	-0.4161	-0.66657
N8	6.379094	-1.372759	-0.577948	-0.42386	-0.34504	-0.6102
C9	4.731991	0.256719	1.805515	0.73481	0.21528	0.66569
O10	4.854277	-0.960577	1.931791	-0.59529	-0.42679	-0.66696
C11	4.768801	1.187199	3.000841	-0.78275	-0.36732	-0.66184
C12	7.742701	-1.785011	-0.883144	-0.05203	-0.23566	-0.37904
H13	4.50082	1.839679	0.507086	0.30859	0.30093	0.40016
H14	3.886745	-0.886808	-0.343746	0.13902	0.17451	0.23982
H16	1.572727	1.085336	-2.410033	0.12658	0.1667	0.22482
H17	1.640939	-0.013882	-1.016562	0.10988	0.14027	0.21208
H18	1.825146	1.731903	-0.788603	0.11306	0.14346	0.1996
H19	5.053804	1.47679	-2.528927	0.34925	0.32424	0.5048
H20	5.938504	-1.700753	0.276857	0.32785	0.32664	0.42689
H21	5.704142	1.025486	3.540609	0.22452	0.17958	0.23345
H22	4.682941	2.242764	2.736028	0.18305	0.12209	0.20359
H23	3.951425	0.919582	3.674129	0.2274	0.1841	0.23542
H24	8.478947	-1.167578	-0.358277	0.0694	0.14533	0.19324
H25	7.914991	-1.68838	-1.954271	0.07968	0.17078	0.21969
H26	7.874072	-2.825896	-0.586121	0.0739	0.13356	0.20082

E[B3LYP/6-311++G(d,p)]:	-609.929913	hartree
E[M05-2X/6-311++G(d,p)]:	-609.839158	hartree
E[M06-2X/6-311++G(d,p)]:	-609.66663	hartree
ZPE[B3LYP/6-311++G(d,p)]:	129.005	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.947	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.71	hartree

Table S4. Coordinates, energetics, and partial charges for model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**3**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	6.165348	-0.893238	-0.853143	0.71288	0.23198	0.66786
N2	5.341059	0.820367	0.644808	-0.33285	-0.29317	-0.62336
C3	4.913677	-0.098694	-0.423979	-0.29078	-0.19359	-0.18731
C4	4.200707	0.559115	-1.577914	0.23456	-0.12665	0.31031
C5	4.912213	1.31394	-2.653765	-0.22656	-0.33604	-0.658
O6	2.928982	0.986406	-1.339273	-0.58685	-0.26131	-0.7066
O7	7.255725	-0.706712	-0.32803	-0.54428	-0.40947	-0.63944
N8	5.941593	-1.822073	-1.809071	-0.42451	-0.29214	-0.61473
C9	4.452026	1.344045	1.518199	0.81701	0.19287	0.67518
O10	3.232924	1.213216	1.367768	-0.62337	-0.4257	-0.67845
C11	5.018426	2.110027	2.692758	-0.80278	-0.36409	-0.65929
C12	7.004606	-2.657173	-2.350917	-0.09292	-0.24336	-0.37728
H13	6.337252	0.822831	0.834594	0.22881	0.29749	0.42322
H14	4.212981	-0.813266	0.029582	0.0967	0.2137	0.23235
H16	4.252984	1.440816	-3.516834	0.09493	0.16394	0.22397
H17	5.195533	2.323987	-2.316639	0.07817	0.15339	0.20863
H18	5.821842	0.805726	-2.981054	0.05274	0.12021	0.20779
H19	2.747921	0.95614	-0.374195	0.45637	0.32887	0.50618
H20	5.03553	-1.818318	-2.255924	0.24962	0.29342	0.39904
H21	4.679115	1.632562	3.614657	0.2224	0.18344	0.23433
H22	6.108426	2.156155	2.690752	0.20745	0.13215	0.20692
H23	4.613008	3.123842	2.68031	0.22157	0.18422	0.23419
H24	7.563703	-2.143126	-3.139338	0.08214	0.15523	0.19336
H25	6.569709	-3.570113	-2.75909	0.09264	0.12437	0.20012
H26	7.698316	-2.915004	-1.551315	0.07693	0.17024	0.22101

E[B3LYP/6-311++G(d,p)]:	-609.928228	hartree
E[M05-2X/6-311++G(d,p)]:	-609.838709	hartree
E[M06-2X/6-311++G(d,p)]:	-609.666599	hartree
ZPE[B3LYP/6-311++G(d,p)]:	128.734	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.973	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.709	hartree

Table S5. Coordinates and energetics for model threonine compound with radical center at C_α, low energy conformation, Structure (**4**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.376862	0.975368	0.168224
N2	4.740279	-0.549463	0.886936
C3	4.938957	0.718482	0.369174
C4	3.812892	1.635516	-0.046999
C5	2.942456	1.03257	-1.162751
O6	3.038233	2.092971	1.055499
O7	7.20315	0.072913	0.362283
N8	6.7634	2.216748	-0.251856
C9	3.632889	-1.130894	1.461188
O10	2.556803	-0.556941	1.593754
C11	3.824055	-2.560947	1.917965
C12	8.176086	2.548722	-0.37984
H13	5.62458	-1.056226	0.935735
H14	4.2655	2.540974	-0.456402
H15	3.55191	0.76808	-2.032154
H16	2.413893	0.143299	-0.816914
H17	2.200213	1.77385	-1.468227
H18	6.106461	2.97645	-0.182252
H19	3.179723	-3.208976	1.317856
H20	4.853599	-2.912655	1.835653
H21	3.4929	-2.64275	2.955098
H22	8.262682	3.523006	-0.861473
H23	8.674822	1.799139	-0.994377
H24	8.679253	2.579809	0.592239
H25	2.610017	1.302095	1.429917

E[B3LYP/6-311++G(d,p)]:	-609.936812	hartree
E[M05-2X/6-311++G(d,p)]:	-609.845051	hartree
E[M06-2X/6-311++G(d,p)]:	-609.672763	hartree
ZPE[B3LYP/6-311++G(d,p)]:	129.497	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.823	kcal/mol

Table S6. Coordinates and energetics for model threonine compound with radical center at C_α, side chain hydrogen bond acceptor, Structure (**5**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.870639	1.419004	0.373486
N2	4.034317	-0.419843	0.599504
C3	4.503871	0.885431	0.527029
C4	3.386058	1.910213	0.628108
C5	2.798001	2.255292	-0.739908
O6	2.30333	1.392386	1.435747
O7	6.010489	2.651109	0.36563
N8	6.925387	0.572317	0.277733
C9	4.559492	-1.663402	0.3216
O10	5.697404	-1.863184	-0.087837
C11	3.607164	-2.816261	0.566525
C12	8.267937	1.095622	0.093457
H13	3.065487	-0.421299	0.910767
H14	3.799952	2.812789	1.078578
H15	2.009729	3.002516	-0.624953
H16	3.57831	2.658816	-1.387273
H17	2.368246	1.367039	-1.211875
H18	6.737123	-0.415986	0.121178
H19	4.026136	-3.456061	1.347477
H20	2.603013	-2.506803	0.86166
H21	3.54596	-3.414982	-0.344735
H22	8.37092	1.621374	-0.861799
H23	8.970268	0.262081	0.120726
H24	8.516544	1.801944	0.888376
H25	2.492612	1.584678	2.360074

E[B3LYP/6-311++G(d,p)]:	-609.931809	hartree
E[M05-2X/6-311++G(d,p)]:	-609.83891	hartree
E[M06-2X/6-311++G(d,p)]:	-609.666244	hartree
ZPE[B3LYP/6-311++G(d,p)]:	129.128	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.952	kcal/mol

Table S7. Coordinates and energetics for model threonine compound with radical center at C_β, Structure (**6**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.83152	0.970844	-2.084056
N2	5.534766	2.368025	-0.24123
C3	5.389314	0.979624	-0.629801
C4	4.5212	0.187392	0.315518
C5	3.169564	0.658788	0.740085
O6	4.766163	-1.161684	0.174579
O7	4.529347	2.006615	-2.664501
N8	4.706292	-0.258466	-2.633957
C9	6.428719	2.764728	0.714586
O10	7.064283	1.973438	1.393684
C11	6.561828	4.26805	0.893257
C12	4.137403	-0.453381	-3.960768
H13	5.170798	3.033825	-0.912572
H14	6.372544	0.494523	-0.634989
H16	2.376118	0.337806	0.043686
H17	2.895601	0.295234	1.734773
H18	3.161669	1.749136	0.775072
H20	4.866321	-1.058189	-2.036988
H21	7.613873	4.541213	0.788265
H22	5.965543	4.844781	0.183741
H23	6.255972	4.527083	1.909653
H24	3.055513	-0.28645	-3.967327
H25	4.342895	-1.473875	-4.285116
H26	4.592386	0.243996	-4.66512
C26	4.280504	-2.035938	1.194461
H27	4.670894	-3.024794	0.957257
H28	4.65211	-1.720943	2.174199
H29	3.187058	-2.072052	1.206414

E[B3LYP/6-311++G(d,p)]:	-649.229782	hartree
E[M05-2X/6-311++G(d,p)]:	-649.13129	hartree
E[M06-2X/6-311++G(d,p)]:	-648.947195	hartree
ZPE[B3LYP/6-311++G(d,p)]:	145.861	kcal/mol
U[B3LYP/6-311++G(d,p)]:	10.214	kcal/mol

Table S8. Coordinates and energetics for model threonine compound with radical center at C_α, low energy conformation, Structure (**7**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.574263	0.877107	1.372015
N2	3.09975	0.723683	-0.457454
C3	4.402077	0.989775	-0.090956
C4	5.438633	1.496326	-1.0713
C5	5.529165	3.024764	-1.079089
O6	6.749282	0.994404	-0.751213
O7	3.605448	0.581392	2.088885
N8	5.810675	1.120321	1.882614
C9	2.479707	0.743434	-1.692994
O10	3.050998	1.038634	-2.731567
C11	1.012791	0.359193	-1.668303
C12	6.072249	0.996916	3.307148
H13	2.540952	0.485971	0.362402
H15	5.161435	1.15976	-2.071317
H16	6.281915	3.342523	-1.803909
H17	4.566072	3.450911	-1.366635
H18	5.803178	3.408805	-0.093845
H20	6.575633	1.200941	1.224012
H21	0.877287	-0.5407	-2.273731
H22	0.620551	0.175786	-0.666519
H23	0.435964	1.157626	-2.140137
H24	5.362749	1.599245	3.877302
H25	7.083633	1.351658	3.506996
H26	5.98159	-0.039459	3.649115
C26	6.971947	-0.3423	-1.186945
H27	7.996712	-0.597385	-0.915311
H28	6.28489	-1.048138	-0.703786
H29	6.856137	-0.420977	-2.274419

E[B3LYP/6-311++G(d,p)]:	-649.247167	hartree
E[M05-2X/6-311++G(d,p)]:	-649.147619	hartree
E[M06-2X/6-311++G(d,p)]:	-648.962857	hartree
ZPE[B3LYP/6-311++G(d,p)]:	146.634	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.937	kcal/mol

Table S9. Coordinates and energetics for model threonine compound with radical center at C_α, side chain hydrogen bond acceptor, Structure (**8**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.159624	0.671094	1.173748
N2	3.733884	0.984783	-0.985107
C3	4.900638	1.03267	-0.232084
C4	6.067899	1.596405	-1.025485
C5	6.787597	0.516545	-1.833215
O6	5.603334	2.585021	-1.960368
O7	6.300617	0.860406	1.618857
N8	4.155776	0.181278	1.943393
C9	2.515721	0.353737	-0.856967
O10	2.203737	-0.371265	0.080054
C11	1.544197	0.630257	-1.986111
C12	4.415212	-0.209297	3.318493
H13	3.854412	1.51907	-1.843015
H15	6.76682	2.046759	-0.317621
H16	7.617357	0.962622	-2.385535
H17	7.180764	-0.249532	-1.16229
H18	6.10721	0.045507	-2.548089
H20	3.303393	-0.127081	1.480232
H21	0.693258	1.188376	-1.586415
H22	1.977666	1.192399	-2.81515
H23	1.161958	-0.322781	-2.356941
H24	3.469966	-0.493078	3.782113
H25	4.854188	0.621444	3.874498
H26	5.111504	-1.052741	3.377054
C26	5.389903	3.865365	-1.373392
H27	6.323141	4.264303	-0.960404
H28	5.035827	4.523198	-2.167396
H29	4.639655	3.824687	-0.573757

E[B3LYP/6-311++G(d,p)]:	-649.241399	hartree
E[M05-2X/6-311++G(d,p)]:	-649.140922	hartree
E[M06-2X/6-311++G(d,p)]:	-648.955859	hartree
ZPE[B3LYP/6-311++G(d,p)]:	146.624	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.88	kcal/mol

Table S10. Coordinates and energetics for model radical compound to study loss of isocyanic acid, Structure (**9**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-1.865401	-1.865973	2.315682
C2	-1.62482	-0.581812	1.545657
O3	-2.157214	0.472993	1.855584
N4	-0.765616	-0.676903	0.487038
C5	-0.458304	0.462211	-0.355004
C6	-0.122911	-0.046975	-1.745641
O7	0.128105	-1.229866	-1.979951
C8	0.680706	1.335031	0.210456
H9	-1.350803	-2.73141	1.893818
H10	-1.534716	-1.721234	3.346566
H11	-2.939213	-2.061881	2.340158
H12	-0.376303	-1.568504	0.215313
H13	-1.357923	1.084653	-0.423531
H14	0.86411	2.191834	-0.439673
H15	0.388944	1.693259	1.198437
H16	1.601961	0.753516	0.299232
N17	0.04283	0.8968	-2.72416
H18	-0.191411	0.488921	-3.634811

E[B3LYP/6-311++G(d,p)]:	-456.003513	hartree
E[M05-2X/6-311++G(d,p)]:	-455.929478	hartree
E[M06-2X/6-311++G(d,p)]:	-455.80154	hartree
ZPE[B3LYP/6-311++G(d,p)]:	89.311	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.583	kcal/mol

Table S11. Coordinates and energetics of model compound to study C_{α}−C bond cleavage from a nitrogen-centered radical, Structure (**10**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-1.287809	-0.769652	2.2447
C2	-0.68451	0.295882	1.345169
O3	-0.202275	1.326081	1.794935
N4	-0.70696	0.021353	0.008881
C5	-0.251415	0.974849	-0.988558
C6	-0.857112	0.58403	-2.336351
O7	-1.520426	-0.430865	-2.484633
C8	1.285365	1.052357	-1.079931
H9	-1.69709	-1.619965	1.695747
H10	-0.517339	-1.125368	2.93259
H11	-2.077886	-0.31409	2.845693
H12	-1.214805	-0.778458	-0.345019
H13	-0.625893	1.970517	-0.72825
H14	1.588577	1.797371	-1.819467
H15	1.68233	1.346078	-0.107961
H16	1.707512	0.081515	-1.355475
N17	-0.679759	1.528027	-3.333652
C18	-0.31758	1.231763	-4.571718
C19	0.147651	-0.144304	-4.999376
H20	0.912828	-0.526273	-4.318813
H21	-0.688364	-0.845782	-4.967973
H22	0.55865	-0.122327	-6.009411
C23	-0.362964	2.277787	-5.501033
H24	-0.054826	2.135769	-6.529381
H25	-0.712132	3.252797	-5.186134

E[B3LYP/6-311++G(d,p)]:	-572.773249	hartree
E[M05-2X/6-311++G(d,p)]:	-572.682546	hartree
E[M06-2X/6-311++G(d,p)]:	-572.516505	hartree
ZPE[B3LYP/6-311++G(d,p)]:	127.628	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.895	kcal/mol

Table S12. Coordinates and energetics of transition state structure for N−C_α bond cleavage from model valine compound with radical center at C_β, Structure (**11**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	7.184429	0.323144	-0.140556
N2	4.545134	1.022129	-1.818169
C3	5.968344	-0.551337	-0.210401
C4	5.805911	-1.648938	-0.989413
C5	4.563686	-2.489515	-0.85206
O7	8.296579	-0.019031	-0.53588
N8	6.9518	1.518697	0.46361
C9	3.688399	1.707668	-0.991859
O10	3.996777	2.066917	0.137912
C11	2.342433	2.096266	-1.599211
C12	7.999943	2.519358	0.570495
H13	4.07695	0.305958	-2.375734
H14	5.188377	-0.311703	0.505336
H16	3.872306	-2.093302	-0.106238
H17	4.037912	-2.578116	-1.810981
H18	4.832569	-3.512112	-0.56045
H20	5.9844	1.811561	0.56729
H21	1.576233	1.428397	-1.19305
H22	2.1052	3.114828	-1.290709
H23	2.328216	2.027872	-2.688343
H24	7.693746	3.276563	1.29346
H25	8.202966	3.004252	-0.391217
H26	8.922147	2.046641	0.909302
C25	6.790526	-2.120153	-2.018587
H27	7.621251	-1.431467	-2.141997
H28	7.196807	-3.094701	-1.719807
H29	6.280763	-2.279428	-2.976825

E[B3LYP/6-311++G(d,p)]:	-573.955245	hartree
E[M05-2X/6-311++G(d,p)]:	-573.851331	hartree
E[M06-2X/6-311++G(d,p)]:	-573.683934	hartree
ZPE[B3LYP/6-311++G(d,p)]:	139.947	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.825	kcal/mol

Table S13. Coordinates and energetics of *z* ion analogue from N−C_α bond cleavage of the model valine compound with radical center at C_β, Structure (**12**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	7.129316	0.403856	-0.292747
C3	5.969678	-0.528558	-0.272521
C4	5.812792	-1.6564	-0.988876
C5	4.558645	-2.479497	-0.831461
O7	8.159418	0.253148	-0.94238
N8	6.96523	1.496758	0.522754
C12	7.962121	2.551729	0.596906
H14	5.165308	-0.251984	0.406007
H16	3.870572	-2.053413	-0.09877
H17	4.033641	-2.566103	-1.789947
H18	4.807086	-3.500791	-0.519728
H20	6.075077	1.641521	0.970673
H24	7.827001	3.110267	1.524485
H25	7.892311	3.243107	-0.250272
H26	8.956379	2.105115	0.585428
C25	6.808726	-2.207001	-1.972254
H27	7.664852	-1.551159	-2.102044
H28	7.16077	-3.187081	-1.627222
H29	6.319827	-2.377044	-2.938931

E[B3LYP/6-311++G(d,p)]:	-365.352931	hartree
E[M05-2X/6-311++G(d,p)]:	-365.286283	hartree
E[M06-2X/6-311++G(d,p)]:	-365.175996	hartree
ZPE[B3LYP/6-311++G(d,p)]:	101.981	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.398	kcal/mol

Table S14. Coordinates and energetics of *c* ion analogue from N−C_α bond cleavage of the model valine compound with radical center at C_β, Structure (**13**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	4.202915	0.613651	-1.66862
C9	3.689298	1.62679	-0.903841
O10	4.416782	2.123501	-0.041267
C11	2.349037	2.186236	-1.287105
H13	4.846479	0.044343	-1.110071
H21	1.647208	1.380505	-1.51439
H22	1.962415	2.81156	-0.483148
H23	2.460198	2.792762	-2.190559

E[B3LYP/6-311++G(d,p)]:	-208.601604	hartree
E[M05-2X/6-311++G(d,p)]:	-208.557567	hartree
E[M06-2X/6-311++G(d,p)]:	-208.499499	hartree
ZPE[B3LYP/6-311++G(d,p)]:	36.944	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.017	kcal/mol

Table S15. Coordinates and energetics of transition state for C_α–C bond cleavage from the model valine compound with radical center at C_β, Structure (**14**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.750299	1.929866	-0.428201
N2	4.298863	1.344311	-1.442136
C3	4.999783	0.480852	-0.544642
C4	5.437897	-0.76538	-0.918561
C5	5.85464	-1.760294	0.126123
O7	6.577922	3.026012	-0.904393
N8	7.852804	1.417343	0.128613
C9	3.041972	1.073829	-1.922461
O10	2.457992	0.020784	-1.726126
C11	2.419487	2.191956	-2.744977
C12	9.120003	2.141044	0.280373
H13	4.679616	2.2756	-1.565334
H14	4.792573	0.646942	0.511269
H16	5.748249	-1.364584	1.139699
H17	5.239536	-2.666838	0.061165
H18	6.89335	-2.089094	-0.017198
H20	7.793518	0.464107	0.451554
H21	2.164065	1.799063	-3.731557
H22	1.488048	2.500799	-2.264739
H23	3.068301	3.062459	-2.861701
H24	9.355184	2.296916	1.336201
H25	9.016082	3.109317	-0.206761
H26	9.934882	1.588575	-0.193283
C25	5.560838	-1.193945	-2.348269
H27	5.389286	-0.367398	-3.03778
H28	6.553544	-1.617588	-2.547124
H29	4.827837	-1.976935	-2.575973

E[B3LYP/6-311++G(d,p)]:	-573.95948	hartree
E[M05-2X/6-311++G(d,p)]:	-573.859515	hartree
E[M06-2X/6-311++G(d,p)]:	-573.691515	hartree
ZPE[B3LYP/6-311++G(d,p)]:	140.66	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.915	kcal/mol

Table S16. Coordinates and energetics of *x* ion analogue from C_α−C bond cleavage of the model valine compound with radical center at C_β, Structure (**15**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.90183	2.076149	-0.300517
O7	6.546426	3.175088	-0.617234
N8	8.106778	1.630604	0.075513
C12	9.313182	2.466525	0.15739
H20	8.182358	0.649395	0.290315
H24	9.729527	2.440101	1.166964
H25	9.031467	3.489849	-0.084399
H26	10.068663	2.126837	-0.555217

E[B3LYP/6-311++G(d,p)]:	-208.614728	hartree
E[M05-2X/6-311++G(d,p)]:	-208.573385	hartree
E[M06-2X/6-311++G(d,p)]:	-208.516259	hartree
ZPE[B3LYP/6-311++G(d,p)]:	38.645	kcal/mol
U[B3LYP/6-311++G(d,p)]:	2.561	kcal/mol

Table S17. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of the model valine compound with radical center at C_β, Structure (**16**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	4.304536	1.327091	-1.290693
C3	4.916748	0.373709	-0.433679
C4	5.394276	-0.815516	-0.815941
C5	5.924918	-1.775613	0.214614
C9	3.187006	1.102684	-2.06732
O10	2.662528	0.011594	-2.189136
C11	2.653402	2.331978	-2.784921
H13	4.568981	2.291216	-1.154612
H14	4.957204	0.672083	0.610498
H16	5.88938	-1.354588	1.221659
H17	5.339304	-2.70225	0.215259
H18	6.960262	-2.055689	-0.009749
H21	2.660576	2.139499	-3.859948
H22	1.613848	2.484151	-2.487099
H23	3.220653	3.243858	-2.585395
C25	5.415876	-1.285041	-2.242392
H27	5.359679	-0.452745	-2.94495
H28	6.329665	-1.854144	-2.44271
H29	4.560377	-1.937205	-2.445697

E[B3LYP/6-311++G(d,p)]:	-365.351507	hartree
E[M05-2X/6-311++G(d,p)]:	-365.286541	hartree
E[M06-2X/6-311++G(d,p)]:	-365.177189	hartree
ZPE[B3LYP/6-311++G(d,p)]:	101.883	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.215	kcal/mol

Table S18. Coordinates, energetics, and partial charges for transition state of N−C_α bond cleavage from model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**17**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	5.266493	-1.168452	-2.375553	0.96106	0.32522	0.63308
N2	5.173214	0.867924	0.28899	-0.61863	-0.15678	-0.41812
C3	3.931358	-0.768478	-1.917157	-0.98832	-0.32406	-0.44167
C4	3.117594	-0.031571	-2.727969	0.77257	0.0101	0.4187
C5	1.729676	0.391177	-2.358954	-0.43752	-0.35788	-0.63124
O6	3.492887	0.376152	-3.938364	-0.63511	-0.26141	-0.67335
O7	5.671554	-0.873383	-3.522943	-0.64358	-0.45577	-0.695
N8	6.028887	-1.882349	-1.515879	-0.66491	-0.35831	-0.61012
C9	4.933408	0.043138	1.37794	0.93095	0.02491	0.60301
O10	5.068678	-1.167108	1.299096	-0.61879	-0.30131	-0.58497
C11	4.58149	0.749317	2.674446	-0.57294	-0.36836	-0.68177
C12	7.404738	-2.233531	-1.831062	-0.01945	-0.25813	-0.37553
H13	4.341114	1.38072	-0.015565	0.33554	0.24456	0.33974
H14	3.561443	-1.124402	-0.965708	0.23659	0.1374	0.22208
H16	1.017918	-0.008792	-3.087029	0.13595	0.17133	0.2311
H17	1.453401	0.040744	-1.364021	0.11478	0.14127	0.20956
H18	1.647083	1.48204	-2.396071	0.12611	0.16989	0.22402
H19	4.413988	-0.002642	-4.079343	0.44776	0.33432	0.50935
H20	5.741009	-1.89227	-0.542783	0.45647	0.32956	0.41938
H21	4.806671	0.084912	3.508672	0.16403	0.16896	0.23946
H22	5.127153	1.688958	2.783222	0.1758	0.1646	0.22851
H23	3.510336	0.97619	2.678923	0.14061	0.17783	0.23031
H24	8.082688	-1.381925	-1.703786	0.05658	0.14808	0.19074
H25	7.467156	-2.565791	-2.866774	0.07843	0.16678	0.21645
H26	7.722729	-3.043362	-1.173066	0.06602	0.12719	0.19627

E[B3LYP/6-311++G(d,p)]:	-609.89993	hartree
E[M05-2X/6-311++G(d,p)]:	-609.797715	hartree
E[M06-2X/6-311++G(d,p)]:	-609.626349	hartree
ZPE[B3LYP/6-311++G(d,p)]:	125.307	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.522	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.685	hartree

Table S19. Coordinates and energetics for *c* ion analogue from N−C_α bond cleavage of model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**18**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	5.163121	1.157235	0.718689
C9	4.833356	0.228976	1.671634
O10	4.520671	-0.900957	1.291758
C11	4.700322	0.700162	3.091574
H13	5.639921	0.699119	-0.064357
H21	5.566418	1.302349	3.376784
H22	3.815566	1.337304	3.176455
H23	4.595985	-0.153238	3.760379

E[B3LYP/6-311++G(d,p)]:	-208.601604	hartree
E[M05-2X/6-311++G(d,p)]:	-208.557631	hartree
E[M06-2X/6-311++G(d,p)]:	-208.499574	hartree
ZPE[B3LYP/6-311++G(d,p)]:	36.94	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.021	kcal/mol

Table S20. Coordinates and energetics for *z* ion analogue from N−C_α bond cleavage of model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**19**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.559351	-0.669799	-1.67673
C3	4.193952	-0.358352	-1.276914
C4	3.433873	0.496083	-2.012487
C5	2.029125	0.872451	-1.668891
O6	3.877689	1.082181	-3.125311
O7	6.080522	-0.177939	-2.697817
N8	6.258481	-1.542465	-0.900068
C12	7.66021	-1.844661	-1.147779
H14	3.773651	-0.805782	-0.385647
H16	1.360975	0.594036	-2.489086
H17	1.69542	0.383527	-0.753726
H18	1.955831	1.956979	-1.544836
H19	4.811962	0.759712	-3.259172
H20	5.852643	-1.823977	-0.022252
H24	8.318864	-1.031769	-0.823932
H25	7.813411	-2.00032	-2.215254
H26	7.926669	-2.755709	-0.610571

E[B3LYP/6-311++G(d,p)]:	-401.295701	hartree
E[M05-2X/6-311++G(d,p)]:	-401.230482	hartree
E[M06-2X/6-311++G(d,p)]:	-401.115765	hartree
ZPE[B3LYP/6-311++G(d,p)]:	88.163	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.734	kcal/mol

Table S21. Coordinates, energetics, and partial charges of transition state for C_α–C bond cleavage from model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**20**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	6.022656	-0.421751	-1.479115	0.40575	0.16881	0.63307
N2	4.639964	0.88857	0.74449	-0.40523	-0.246	-0.60121
C3	4.175354	0.219392	-0.417277	-0.23172	-0.15106	-0.1245
C4	3.501414	0.954439	-1.368491	0.35911	-0.0827	0.29675
C5	2.852392	0.376658	-2.575718	-0.48244	-0.36615	-0.64262
O6	3.61148	2.327728	-1.283498	-0.60032	-0.26301	-0.71267
O7	6.27485	0.015942	-2.573767	-0.46426	-0.34278	-0.6078
N8	6.609543	-1.422813	-0.809082	-0.34926	-0.35124	-0.67301
C9	5.202416	0.257896	1.808692	0.73053	0.19178	0.66608
O10	5.397491	-0.957322	1.827503	-0.59146	-0.42015	-0.6718
C11	5.578839	1.138159	2.981758	-0.69859	-0.36977	-0.661
C12	7.791008	-2.136294	-1.301897	-0.05585	-0.24178	-0.38419
H13	4.567956	1.895512	0.741053	0.31966	0.30482	0.41128
H14	3.906167	-0.81519	-0.256042	0.13956	0.15722	0.23631
H16	3.421481	0.622546	-3.483949	0.14108	0.16992	0.21923
H17	2.808814	-0.711276	-2.506309	0.15262	0.15328	0.22694
H18	1.830262	0.753391	-2.702312	0.12903	0.15711	0.21212
H19	3.550243	2.721398	-2.160657	0.42858	0.28797	0.47781
H20	6.283578	-1.579963	0.140925	0.29276	0.33641	0.43212
H21	6.650718	1.036812	3.166695	0.19216	0.17735	0.23104
H22	5.337496	2.192267	2.832551	0.17539	0.12233	0.20266
H23	5.058574	0.775123	3.870788	0.20473	0.18003	0.23349
H24	8.718295	-1.662352	-0.964692	0.06359	0.14447	0.18995
H25	7.775751	-2.13603	-2.391564	0.08689	0.15456	0.21214
H26	7.767615	-3.166199	-0.941517	0.05772	0.12855	0.1978

E[B3LYP/6-311++G(d,p)]:	-609.889145	hartree
E[M05-2X/6-311++G(d,p)]:	-609.789475	hartree
E[M06-2X/6-311++G(d,p)]:	-609.618271	hartree
ZPE[B3LYP/6-311++G(d,p)]:	126.42	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.528	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.672	hartree

Table S22. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**21**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	4.6282	0.868781	0.764489
C3	4.134966	0.218991	-0.371664
C4	3.596641	0.885289	-1.396242
C5	3.04787	0.265754	-2.638064
O6	3.503835	2.265045	-1.281844
C9	5.207286	0.206286	1.817136
O10	5.31687	-1.008041	1.844449
C11	5.693413	1.086224	2.950429
H13	4.579287	1.876598	0.776115
H14	4.217157	-0.856529	-0.356502
H16	3.564849	0.638057	-3.532332
H17	3.168628	-0.817812	-2.61271
H18	1.980433	0.48829	-2.75455
H19	3.345085	2.654168	-2.146771
H21	6.750983	0.879145	3.126231
H22	5.563814	2.154412	2.762907
H23	5.151445	0.817257	3.859972

E[B3LYP/6-311++G(d,p)]:	-401.280592	hartree
E[M05-2X/6-311++G(d,p)]:	-401.21494	hartree
E[M06-2X/6-311++G(d,p)]:	-401.101337	hartree
ZPE[B3LYP/6-311++G(d,p)]:	87.417	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.072	kcal/mol

Table S23. Coordinates and energetics of *x* ion analogue from C_α−C bond cleavage of model threonine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**22**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.730929	-0.37736	-1.78939
O7	6.969644	-0.110046	-2.931304
N8	7.10323	-1.436272	-1.062941
C12	7.964661	-2.516083	-1.564277
H20	6.806054	-1.4567	-0.100979
H24	9.015273	-2.333406	-1.322377
H25	7.85591	-2.573266	-2.646526
H26	7.652515	-3.463351	-1.122781

E[B3LYP/6-311++G(d,p)]:	-208.614689	hartree
E[M05-2X/6-311++G(d,p)]:	-208.572959	hartree
E[M06-2X/6-311++G(d,p)]:	-208.516435	hartree
ZPE[B3LYP/6-311++G(d,p)]:	38.683	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.127	kcal/mol

Table S24. Coordinates, energetics, and partial charges for transition state of N−C_α bond cleavage from model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**23**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	5.816617	-1.086171	-1.787345	0.94508	0.23282	0.30926
N2	5.429026	0.563575	0.507423	-0.60096	-0.39397	-0.50807
C3	4.659096	-0.32811	-1.239526	-0.86595	-0.27927	-0.23967
C4	4.072038	0.77565	-1.904379	0.78398	0.07402	0.12684
C5	4.529326	1.366031	-3.196186	-0.43612	-0.33799	-0.32053
O6	3.071984	1.380791	-1.333368	-0.64096	-0.26352	-0.37801
O7	6.627624	-0.617113	-2.578111	-0.56999	-0.37277	-0.32771
N8	5.924152	-2.361165	-1.302779	-0.58548	-0.26902	-0.31274
C9	4.508786	0.87052	1.396739	0.75408	0.10326	0.31704
O10	3.280215	0.97079	1.094222	-0.68583	-0.43694	-0.35906
C11	4.88909	1.12708	2.844053	-0.64381	-0.34943	-0.33453
C12	6.977432	-3.266619	-1.732724	-0.0898	-0.28144	-0.18861
H13	6.390015	0.460138	0.811354	0.31182	0.25252	0.18501
H14	3.988614	-0.869354	-0.582756	0.25316	0.18353	0.11204
H16	3.666412	1.792971	-3.71116	0.13042	0.15537	0.11119
H17	5.228186	2.184171	-2.983885	0.14638	0.18713	0.11035
H18	5.053614	0.647574	-3.820181	0.11807	0.16898	0.12087
H19	3.051658	1.157209	-0.285791	0.54164	0.42814	0.2488
H20	5.199069	-2.714266	-0.699032	0.35168	0.26139	0.1931
H21	4.334268	0.431469	3.478529	0.19194	0.1743	0.11293
H22	5.957676	1.013864	3.032516	0.14812	0.11567	0.10083
H23	4.578433	2.138272	3.116044	0.18976	0.17734	0.11583
H24	6.694636	-3.826196	-2.630828	0.06882	0.15866	0.09511
H25	7.200277	-3.971996	-0.930688	0.09257	0.12451	0.09767
H26	7.869726	-2.685042	-1.962042	0.09138	0.1867	0.11205

E[B3LYP/6-311++G(d,p)]:	-609.897912	hartree
E[M05-2X/6-311++G(d,p)]:	-609.798955	hartree
E[M06-2X/6-311++G(d,p)]:	-609.62561	hartree
ZPE[B3LYP/6-311++G(d,p)]:	125.596	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.053	kcal/mol
Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.683	hartree

Table S25. Coordinates and energetics for *c* ion analogue from N−C_α bond cleavage of model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**24**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	5.353403	0.485923	0.360328
C9	4.611479	0.868321	1.315734
O10	3.309354	1.161255	1.06913
C11	4.946982	1.067843	2.767046
H13	6.302312	0.298401	0.672611
H19	3.166064	1.013115	0.122691
H21	4.303025	0.439608	3.387474
H22	5.989517	0.821807	2.965748
H23	4.760972	2.106652	3.051448

E[B3LYP/6-311++G(d,p)]:	-209.268494	hartree
E[M05-2X/6-311++G(d,p)]:	-209.230874	hartree
E[M06-2X/6-311++G(d,p)]:	-209.17204	hartree
ZPE[B3LYP/6-311++G(d,p)]:	46.439	kcal/mol
U[B3LYP/6-311++G(d,p)]:	2.881	kcal/mol

Table S26. Coordinates and energetics for *z* ion analogue from N−C_α bond cleavage of model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**25**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.665629	-1.336534	-2.179358
C3	4.442663	-0.660419	-1.717515
C4	3.885796	0.58602	-2.228286
C5	4.550362	1.347632	-3.348642
O6	2.845615	0.992533	-1.70446
O7	6.385246	-0.915318	-3.081583
N8	5.948904	-2.499544	-1.513376
C12	7.124267	-3.290203	-1.841064
H14	3.864615	-1.103545	-0.911849
H16	3.959752	2.238028	-3.561262
H17	5.57186	1.622358	-3.075982
H18	4.637358	0.723739	-4.241009
H20	5.338744	-2.807643	-0.773987
H24	7.105689	-3.590648	-2.891446
H25	7.136163	-4.180075	-1.212427
H26	8.039537	-2.716796	-1.671726

E[B3LYP/6-311++G(d,p)]:	-400.636158	hartree
E[M05-2X/6-311++G(d,p)]:	-400.568143	hartree
E[M06-2X/6-311++G(d,p)]:	-400.455537	hartree
ZPE[B3LYP/6-311++G(d,p)]:	78.934	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.15	kcal/mol

Table S27. Coordinates, energetics, and partial charges of transition state for C_α−C bond cleavage from model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**26**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]	ESP-Derived Charge	Mulliken Charge	NBO 5.0 Natural Charge
C1	6.437539	-1.304603	-0.810741	0.34054	0.16314	0.61506
N2	5.336574	0.770932	0.591475	-0.17254	-0.23597	-0.65978
C3	4.614833	0.006213	-0.36895	-0.44648	-0.24006	-0.12336
C4	4.188876	0.554908	-1.550137	0.45876	-0.01768	0.3361
C5	4.709435	1.786522	-2.198785	-0.19065	-0.34693	-0.63543
O6	3.284737	-0.119801	-2.334788	-0.6102	-0.22798	-0.6893
O7	7.397769	-1.149851	-0.092963	-0.4005	-0.3562	-0.61098
N8	6.351549	-1.989621	-1.958699	-0.39213	-0.29777	-0.65293
C9	4.713496	1.637645	1.457429	0.75687	0.17193	0.66838
O10	3.531946	1.926806	1.373154	-0.60358	-0.37211	-0.62352
C11	5.615817	2.236336	2.523548	-0.7388	-0.37848	-0.66774
C12	7.478282	-2.684299	-2.591739	0.14508	-0.25389	-0.38699
H13	6.275572	0.450961	0.806448	0.16401	0.25643	0.41419
H14	4.043484	-0.836123	0.023961	0.13933	0.1425	0.19595
H16	5.128621	1.554056	-3.185199	0.08542	0.15391	0.2159
H17	3.898362	2.505838	-2.3501	0.07868	0.17085	0.22929
H18	5.480419	2.248297	-1.583874	0.03909	0.15885	0.22748
H19	2.793303	-0.747771	-1.791141	0.4175	0.28466	0.47253
H20	5.478923	-1.924658	-2.460564	0.26983	0.29361	0.39885
H21	5.210627	1.98615	3.506746	0.20543	0.17578	0.2302
H22	6.649591	1.890854	2.46204	0.1804	0.13562	0.20341
H23	5.594524	3.324309	2.428253	0.20016	0.17745	0.22996
H24	7.849839	-2.128861	-3.457526	0.02276	0.14394	0.19394
H25	7.17107	-3.6826	-2.908756	0.00854	0.13289	0.19755
H26	8.278376	-2.77206	-1.858189	0.04246	0.1655	0.22122
			E[B3LYP/6-311++G(d,p)]:	-609.882024	hartree	
			E[M05-2X/6-311++G(d,p)]:	-609.782188	hartree	
			E[M06-2X/6-311++G(d,p)]:	-609.611014	hartree	
			ZPE[B3LYP/6-311++G(d,p)]:	126.301	kcal/mol	
			U[B3LYP/6-311++G(d,p)]:	9.649	kcal/mol	
			Utot (SCFE + ZPE + U)[B3LYP/6-311++G(d,p)]:	-609.665	hartree	

Table S28. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**27**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	5.01786	0.599519	0.791945
C3	4.191346	-0.040361	-0.17256
C4	4.024383	0.425937	-1.417483
C5	4.684231	1.623544	-2.013453
O6	3.176723	-0.172022	-2.307009
C9	4.608967	1.67278	1.555168
O10	3.549034	2.243998	1.38311
C11	5.594025	2.110428	2.627444
H13	5.874804	0.139913	1.063047
H14	3.632211	-0.912365	0.163679
H16	5.145864	1.35621	-2.968193
H17	3.936591	2.397549	-2.209538
H18	5.440602	2.028505	-1.344199
H19	2.711691	-0.900588	-1.878729
H21	5.116236	2.003597	3.604085
H22	6.529297	1.546346	2.625575
H23	5.816132	3.169809	2.485865

E[B3LYP/6-311++G(d,p)]:	-401.271343	hartree
E[M05-2X/6-311++G(d,p)]:	-401.206769	hartree
E[M06-2X/6-311++G(d,p)]:	-401.093651	hartree
ZPE[B3LYP/6-311++G(d,p)]:	87.152	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.506	kcal/mol

Table S29. Coordinates and energetics of *x* ion analogue from C_α−C bond cleavage of model threonine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**28**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.194632	-0.917847	-0.86435
O7	7.1345	-0.793526	-0.133703
N8	6.016788	-1.721128	-1.920205
C12	7.034375	-2.647211	-2.437193
H20	5.138636	-1.644527	-2.40765
H24	7.430474	-2.300276	-3.395066
H25	6.60752	-3.644469	-2.561375
H26	7.846769	-2.695029	-1.71401

E[B3LYP/6-311++G(d,p)]:	-208.613429	hartree
E[M05-2X/6-311++G(d,p)]:	-208.571743	hartree
E[M06-2X/6-311++G(d,p)]:	-208.514801	hartree
ZPE[B3LYP/6-311++G(d,p)]:	38.704	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.111	kcal/mol

Table S30. Coordinates and energetics of transition state of water loss from model threonine compound with radical center at C_α, Structure (**29**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.005182	0.735993	1.255903
N2	3.75746	0.761614	-1.044956
C3	4.85342	0.788537	-0.235624
C4	6.008686	1.308878	-0.955298
C5	6.605671	0.534683	-2.092545
O6	5.147126	2.580612	-1.953732
O7	5.982131	1.290177	1.776696
N8	4.062132	0.083667	1.961491
C9	2.570054	0.110268	-0.869369
O10	2.335172	-0.742995	-0.005455
C11	1.48765	0.483044	-1.86293
C12	4.150374	-0.025797	3.407337
H13	4.283833	1.942022	-1.845009
H14	6.712885	1.861508	-0.339878
H15	7.251433	1.164522	-2.706134
H16	7.219562	-0.263587	-1.659919
H17	5.835305	0.073608	-2.712569
H18	3.334354	-0.406179	1.437134
H19	0.685576	1.004978	-1.331889
H20	1.8544	1.116807	-2.670197
H21	1.055404	-0.429899	-2.278035
H22	3.280776	-0.576933	3.765531
H23	4.16624	0.962139	3.874424
H24	5.059843	-0.552723	3.711257
H25	5.000229	3.351203	-1.387005

E[B3LYP/6-311++G(d,p)]:	-609.8742	hartree
E[M05-2X/6-311++G(d,p)]:	-609.776697	hartree
E[M06-2X/6-311++G(d,p)]:	-609.602812	hartree
ZPE[B3LYP/6-311++G(d,p)]:	125.813	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.763	kcal/mol

Table S31. Coordinates and energetics of nitrogen-centered radical product of water loss from model threonine compound with radical center at C_{α}, Structure (**30**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.747454	1.091158	0.76192
N2	3.996932	-0.501173	-0.165173
C3	4.385994	0.712195	0.16303
C4	3.47904	1.781331	0.05554
C5	2.10579	1.668425	-0.493163
O7	5.808379	1.97178	1.611367
N8	6.825106	0.435845	0.283016
C9	4.708343	-1.669938	-0.307699
O10	5.660256	-1.782031	-1.073575
C11	4.128981	-2.844859	0.444523
C12	8.161905	0.737009	0.775659
H15	3.824407	2.744262	0.414317
H16	1.371277	1.971715	0.264225
H17	1.973358	2.36006	-1.334262
H18	1.880967	0.654498	-0.82182
H20	6.696714	-0.271544	-0.433569
H21	4.025475	-2.603832	1.506537
H22	3.129123	-3.069157	0.064118
H23	4.773632	-3.713908	0.318325
H24	8.37407	1.804179	0.681032
H25	8.883828	0.170498	0.188218
H26	8.263308	0.465271	1.829655

E[B3LYP/6-311++G(d,p)]:	-533.450622	hartree
E[M05-2X/6-311++G(d,p)]:	-533.362788	hartree
E[M06-2X/6-311++G(d,p)]:	-533.210783	hartree
ZPE[B3LYP/6-311++G(d,p)]:	110.21	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.267	kcal/mol

Table S32. Coordinates and energetics of transition state for loss of methanol from model O-methyl threonine compound with radical center at C_α, Structure (**31**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.99782	0.751798	1.242817
N2	3.752321	0.734939	-1.05858
C3	4.845449	0.789239	-0.248351
C4	5.998225	1.314492	-0.972636
C5	6.577286	0.538019	-2.120142
O6	5.18914	2.613091	-1.904515
O7	5.96467	1.326237	1.764018
N8	4.065636	0.089008	1.95453
C9	2.577249	0.070358	-0.869539
O10	2.352198	-0.779757	0.0032
C11	1.485167	0.413683	-1.86488
C12	4.159164	-0.013876	3.400064
H13	4.335769	2.019343	-1.891175
H15	6.716901	1.840631	-0.350433
H16	7.233208	1.159189	-2.732696
H17	7.175542	-0.277286	-1.698293
H18	5.794324	0.097768	-2.739702
H20	3.347069	-0.418833	1.433088
H21	0.672401	0.922579	-1.337362
H22	1.839792	1.048847	-2.676539
H23	1.071695	-0.510828	-2.274217
H24	3.305377	-0.58761	3.761397
H25	4.14907	0.974753	3.866579
H26	5.083073	-0.515352	3.703544
C26	4.941482	3.819531	-1.150761
H27	5.872735	4.382291	-1.115305
H28	4.178338	4.396856	-1.674522
H29	4.606519	3.578357	-0.139516

E[B3LYP/6-311++G(d,p)]:	-649.18607	hartree
E[M05-2X/6-311++G(d,p)]:	-649.081442	hartree
E[M06-2X/6-311++G(d,p)]:	-648.895155	hartree
ZPE[B3LYP/6-311++G(d,p)]:	144.194	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.805	kcal/mol

Table S33. Coordinates and energetics of nitrogen-centered radical product results from loss of methanol from model O-methyl threonine compound with radical center at C_α, Structure (**32**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.464451	1.166236	0.997253
N2	3.8356	0.023521	-1.184309
C3	4.666887	0.746608	-0.465666
C4	5.820041	1.279017	-1.068902
C5	6.234699	1.018559	-2.468568
O7	4.835375	2.274607	1.364455
N8	3.903654	0.253394	1.816619
C9	2.747746	-0.734385	-0.819766
O10	2.81384	-1.646756	-0.002015
C11	1.49838	-0.452807	-1.62072
C12	3.686737	0.547413	3.225962
H15	6.427648	1.932476	-0.453176
H16	6.294657	1.962485	-3.02579
H17	7.24415	0.589769	-2.493582
H18	5.545334	0.347047	-2.978689
H20	3.63825	-0.651619	1.441167
H21	0.664666	-1.019997	-1.208784
H22	1.269153	0.616372	-1.612944
H23	1.659414	-0.742933	-2.662419
H24	3.324182	-0.355349	3.716782
H25	2.950981	1.345878	3.352604
H26	4.617485	0.869294	3.698058

E[B3LYP/6-311++G(d,p)]:	-533.450637	hartree
E[M05-2X/6-311++G(d,p)]:	-533.362794	hartree
E[M06-2X/6-311++G(d,p)]:	-533.210782	hartree
ZPE[B3LYP/6-311++G(d,p)]:	110.217	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.271	kcal/mol

Table S34. Coordinates and energetics of transition state for C_{α}–C bond cleavage from a model nitrogen-centered radical, Structure (**33**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-1.589713	0.807606	2.182177
C2	-1.00158	1.220277	0.85057
O3	-1.434605	2.142248	0.187932
N4	0.082064	0.461482	0.417122
C5	0.620633	0.574181	-0.85701
C6	-0.673985	-0.422712	-2.093293
O7	-1.198432	-1.261751	-1.421634
C8	1.942712	-0.106682	-1.074844
H11	-0.90276	0.213754	2.788571
H12	-1.882727	1.702674	2.731112
H13	-2.491845	0.216218	1.998095
H14	0.294331	-0.377554	0.939621
H15	0.47493	1.559817	-1.287824
H16	2.234905	-0.049084	-2.123345
H17	2.725751	0.375704	-0.47567
H18	1.903029	-1.162782	-0.789456
N17	-0.484611	0.020914	-3.253903
C18	-0.299342	1.255163	-3.840497
C21	0.506015	1.204569	-5.115239
H22	1.510354	0.813402	-4.924099
H23	0.031449	0.531711	-5.835196
H24	0.593297	2.193554	-5.566377
C24	-0.834904	2.396667	-3.357653
H25	-0.671146	3.33346	-3.875637
H26	-1.427905	2.417376	-2.451163

E[B3LYP/6-311++G(d,p)]:	-572.743398	hartree
E[M05-2X/6-311++G(d,p)]:	-572.645775	hartree
E[M06-2X/6-311++G(d,p)]:	-572.481657	hartree
ZPE[B3LYP/6-311++G(d,p)]:	137.652	kcal/mol
U[B3LYP/6-311++G(d,p)]:	7.82	kcal/mol

Table S35. Coordinates and energetics of *a* ion analogue from C_α–C bond cleavage of a model nitrogen-centered radical, Structure (**34**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-1.445372	1.134147	2.355712
C2	-0.808081	1.485265	1.026206
O3	-1.234666	2.372297	0.305108
N4	0.294569	0.726756	0.671559
C5	0.985558	0.864374	-0.517497
C8	2.255668	0.119045	-0.720061
H11	-0.91599	0.352375	2.905345
H12	-1.490555	2.033437	2.973555
H13	-2.473223	0.806903	2.180384
H14	0.590954	0.004086	1.311674
H15	0.65541	1.674056	-1.149455
H16	2.561327	0.166784	-1.766542
H17	3.087209	0.523814	-0.120259
H18	2.159046	-0.941661	-0.453652

E[B3LYP/6-311++G(d,p)]:	-287.277927	hartree
E[M05-2X/6-311++G(d,p)]:	-287.221181	hartree
E[M06-2X/6-311++G(d,p)]:	-287.135918	hartree
ZPE[B3LYP/6-311++G(d,p)]:	72.584	kcal/mol
U[B3LYP/6-311++G(d,p)]:	4.959	kcal/mol

Table S36. Coordinates and energetics of *x* ion analogue from C_α–C bond cleavage of a model nitrogen-centered radical, Structure (**35**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C6	-0.616135	-0.514306	-2.110091
O7	-0.881819	-1.159781	-1.170525
N17	-0.294791	0.041758	-3.12601
C18	-0.311782	1.295294	-3.758914
C21	0.307565	1.270878	-5.12611
H22	1.348979	0.940029	-5.068768
H23	-0.221105	0.564183	-5.772872
H24	0.276302	2.259255	-5.584488
C24	-0.832465	2.381912	-3.180481
H25	-0.826563	3.330011	-3.701828
H26	-1.270553	2.353627	-2.190391

E[B3LYP/6-311++G(d,p)]:	-285.47993	hartree
E[M05-2X/6-311++G(d,p)]:	-285.429314	hartree
E[M06-2X/6-311++G(d,p)]:	-285.351032	hartree
ZPE[B3LYP/6-311++G(d,p)]:	52.305	kcal/mol
U[B3LYP/6-311++G(d,p)]:	4.044	kcal/mol

Table S37. Coordinates and energetics of low-energy conformation of the threonine model compound, Structure (**S1**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.215571	-0.855925	-0.193318
N2	3.746757	-0.861199	-0.27515
C3	4.926793	-0.000594	-0.260417
C4	4.852323	0.964745	0.938885
C5	3.707128	1.96114	0.83791
O6	4.686736	0.222885	2.147331
O7	6.851813	-0.982555	0.85266
N8	6.561371	-1.435042	-1.362164
C9	3.274116	-1.447009	-1.405068
O10	3.835923	-1.315286	-2.491923
C11	2.010492	-2.268252	-1.257481
C12	7.682104	-2.357273	-1.474158
H13	3.33043	-1.05855	0.624473
H14	4.93234	0.567642	-1.194347
H15	5.803152	1.510501	0.969104
H16	3.715519	2.613467	1.712965
H17	3.80749	2.578874	-0.058312
H18	2.740468	1.4536	0.802078
H19	5.49435	-0.309276	2.23443
H20	5.882256	-1.378784	-2.116219
H21	1.239693	-1.836927	-1.899649
H22	2.205372	-3.281207	-1.614956
H23	1.637784	-2.311946	-0.232763
H24	8.090799	-2.307147	-2.484154
H25	7.381443	-3.389026	-1.263431
H26	8.45036	-2.069985	-0.757901

E[B3LYP/6-311++G(d,p)]:	-610.586077	hartree
E[M05-2X/6-311++G(d,p)]:	-610.499402	hartree
E[M06-2X/6-311++G(d,p)]:	-610.325806	hartree
ZPE[B3LYP/6-311++G(d,p)]:	137.647	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.836	kcal/mol

Table S38. Coordinates and energetics of *N*-methylacetamide radical, Structure (**S2**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	1.409618	1.207138	-0.126069
H2	2.381643	0.729567	-0.084079
H5	1.349027	2.281793	-0.222037
C5	0.16289	0.460084	-0.056875
O6	-0.939248	1.006975	-0.107047
N7	0.284309	-0.903127	0.06699
H9	1.200673	-1.316997	0.10871
C9	-0.886197	-1.759863	0.147578
H10	-0.558989	-2.794304	0.253123
H11	-1.507878	-1.490286	1.005364
H12	-1.50019	-1.667586	-0.752252

E[B3LYP/6-311++G(d,p)]:	-247.939853	hartree
E[M05-2X/6-311++G(d,p)]:	-247.89241	hartree
E[M06-2X/6-311++G(d,p)]:	-247.820812	hartree
ZPE[B3LYP/6-311++G(d,p)]:	54.812	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.587	kcal/mol

Table S39. Coordinates and energetics of transition state for hydrogen atom abstraction from C_α of threonine model compound by *N*-methylacetamide radical, Structure (**S3**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.023508	-1.099657	-0.346762
N2	3.621398	-0.80428	0.199747
C3	4.833009	-0.137603	-0.166624
C4	5.19299	0.917859	0.904101
C5	4.235483	2.103098	0.973106
O6	5.188118	0.299254	2.195089
O7	6.403788	-1.713144	0.668017
N8	6.642534	-1.175785	-1.528429
C9	2.955666	-1.694083	-0.600856
O10	3.270255	-1.877153	-1.775718
C11	1.807851	-2.440195	0.056175
C12	7.792374	-2.050526	-1.720067
H13	3.3652	-0.734833	1.17999
H14	4.591212	0.53158	-1.313894
H15	6.203697	1.285781	0.67276
H16	4.523859	2.742406	1.813446
H17	4.274718	2.697522	0.055018
H18	3.202623	1.775339	1.134301
H19	5.7481	-0.502584	2.114083
H20	6.248708	-0.722945	-2.358495
H21	0.966264	-2.486628	-0.640399
H22	2.12886	-3.468819	0.258163
H23	1.476916	-1.989703	0.997432
H24	8.172878	-1.893522	-2.731321
H25	7.511099	-3.10265	-1.596419
H26	8.575923	-1.818473	-0.992301
C27	4.309926	1.310596	-2.433054
H2	3.317418	1.712089	-2.221221
H4	5.104991	2.053014	-2.362549
C30	4.455341	0.415423	-3.607614
O31	5.571009	-0.022125	-3.943939
N7	3.322581	0.089303	-4.286266
H9	2.442428	0.313333	-3.842172
C34	3.312863	-0.981765	-5.274149
H10	2.398725	-0.905869	-5.869022
H11	4.179164	-0.871601	-5.928982
H12	3.357604	-1.965397	-4.790087

E[B3LYP/6-311++G(d,p)]:	-858.504351	hartree
E[M05-2X/6-311++G(d,p)]:	-858.372809	hartree
E[M06-2X/6-311++G(d,p)]:	-858.129654	hartree
ZPE[B3LYP/6-311++G(d,p)]:	191.137	kcal/mol
U[B3LYP/6-311++G(d,p)]:	12.673	kcal/mol

Table S40. Coordinates and energetics of N-methylacetamide, Structure (**S4**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	1.417452	1.281892	0
H2	2.326272	0.676082	0
H4	1.420185	1.927804	0.880403
H5	1.420185	1.927804	-0.880403
C5	0.136839	0.464771	0
O6	-0.966722	0.988238	0
N7	0.292412	-0.890526	0
H9	1.220254	-1.279928	0
C9	-0.853964	-1.788176	0
H10	-0.494842	-2.817597	0
H11	-1.475516	-1.625325	0.883601
H12	-1.475516	-1.625325	-0.883601

E[B3LYP/6-311++G(d,p)]:	-248.605926	hartree
E[M05-2X/6-311++G(d,p)]:	-248.558138	hartree
E[M06-2X/6-311++G(d,p)]:	-248.486013	hartree
ZPE[B3LYP/6-311++G(d,p)]:	63.531	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.678	kcal/mol

Table S41. Coordinates and energetics of transition state for hydrogen atom abstraction from C_β of the threonine model compound by *N*-methylacetamide radical, Structure (**S5**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.032807	-0.693691	0.223863
N2	3.662028	-0.875666	-0.463058
C3	4.75917	0.068253	-0.217762
C4	4.335654	1.111252	0.81926
C5	3.218711	2.037172	0.401438
O6	4.057935	0.542282	2.062394
O7	6.425685	-0.683998	1.397148
N8	6.662905	-1.359473	-0.755255
C9	3.513567	-1.540397	-1.639865
O10	4.344171	-1.452961	-2.542725
C11	2.271723	-2.394938	-1.782413
C12	7.830966	-2.188099	-0.486855
H13	3.003102	-1.015654	0.289373
H14	4.971119	0.567961	-1.16676
H15	5.402352	1.898387	0.951071
H16	3.052973	2.780872	1.183261
H17	3.472666	2.557459	-0.525212
H18	2.280548	1.492493	0.245735
H19	4.838624	0.009437	2.298151
H20	6.195593	-1.409527	-1.657728
H21	1.700824	-2.031913	-2.639587
H22	2.576344	-3.420349	-2.001473
H23	1.631299	-2.38886	-0.898567
H24	8.258486	-2.508227	-1.436653
H25	7.565993	-3.069145	0.104625
H26	8.573978	-1.615377	0.069576
C27	6.528921	2.726491	1.057702
H2	7.247025	2.190612	0.437952
H4	6.19326	3.667347	0.631077
C30	6.864964	2.837816	2.503768
O31	6.628885	3.850974	3.156851
N7	7.458356	1.732021	3.051432
H9	7.418501	0.868196	2.527017
C34	7.74236	1.660096	4.474978
H10	8.36026	0.781578	4.666677
H11	8.284687	2.552699	4.790059
H12	6.828647	1.593431	5.07667

E[B3LYP/6-311++G(d,p)]:	-858.50997	hartree
E[M05-2X/6-311++G(d,p)]:	-858.377791	hartree
E[M06-2X/6-311++G(d,p)]:	-858.134289	hartree
ZPE[B3LYP/6-311++G(d,p)]:	190.996	kcal/mol
U[B3LYP/6-311++G(d,p)]:	13.315	kcal/mol

Table S42. Coordinates and energetics of ground state conformation of the serine model compound, Structure (**S6**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.008102	0.802425	-0.21862
N2	4.195431	-0.518356	0.842632
C3	4.583425	0.213248	-0.361697
C4	3.562684	1.324929	-0.620374
O5	3.434209	2.187718	0.50075
O6	6.190965	2.00665	-0.041742
N7	7.002598	-0.103837	-0.30306
C8	4.573411	-1.799694	1.085693
O9	5.303711	-2.421767	0.315374
C10	4.044742	-2.425245	2.359151
C11	8.397309	0.258985	-0.093698
H12	3.674546	0.006586	1.531773
H13	4.575952	-0.495033	-1.195934
H14	3.853622	1.879191	-1.51955
H15	4.293202	2.630562	0.585676
H16	6.731954	-1.083317	-0.321752
H17	3.485164	-3.325677	2.097304
H18	4.892719	-2.73359	2.974432
H19	3.401747	-1.759123	2.937099
H20	9.030429	-0.542543	-0.474874
H21	8.620186	0.417068	0.966678
H22	8.620985	1.181661	-0.629446
H23	2.579774	0.879816	-0.789938

E[B3LYP/6-311++G(d,p)]:	-571.257548	hartree
E[M05-2X/6-311++G(d,p)]:	-571.176616	hartree
E[M06-2X/6-311++G(d,p)]:	-571.016729	hartree
ZPE[B3LYP/6-311++G(d,p)]:	120.318	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.495	kcal/mol

Table S43. Coordinates and energetics of transition state for hydrogen atom abstraction from C_β of the serine model compound by *N*-methylacetamide radical, Structure (**S7**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.057613	-0.723023	0.21991
N2	3.673187	-0.887804	-0.450358
C3	4.779321	0.044244	-0.197938
C4	4.369592	1.05785	0.85675
O5	4.075635	0.50993	2.098005
O6	6.470718	-0.706595	1.38583
N7	6.664397	-1.392703	-0.771282
C8	3.515255	-1.534683	-1.636416
O9	4.349269	-1.445673	-2.536181
C10	2.258311	-2.362298	-1.791146
C11	7.836531	-2.227524	-0.541314
H12	3.007108	-1.019079	0.297074
H13	4.981691	0.566193	-1.137488
H14	5.403002	1.9168	0.964555
H15	4.853592	-0.014409	2.355414
H16	6.179627	-1.429802	-1.665147
H17	1.672002	-1.949773	-2.615192
H18	2.538685	-3.380638	-2.066022
H19	1.640173	-2.386558	-0.892278
H20	8.253375	-2.514395	-1.505943
H21	7.581669	-3.129431	0.02265
H22	8.586281	-1.672761	0.023696
C23	6.50264	2.744678	1.050427
H24	7.228869	2.214476	0.435237
H25	6.161551	3.681075	0.618674
C26	6.840789	2.870269	2.496443
O27	6.627894	3.898737	3.132412
N28	7.403605	1.759924	3.064055
H29	7.378972	0.892593	2.544417
C30	7.697173	1.711847	4.486715
H31	8.31636	0.837329	4.690537
H32	8.239426	2.610845	4.781916
H33	6.786764	1.655632	5.094034
H34	3.542549	1.691606	0.53629

E[B3LYP/6-311++G(d,p)]:	-819.178724	hartree
E[M05-2X/6-311++G(d,p)]:	-819.051687	hartree
E[M06-2X/6-311++G(d,p)]:	-818.821808	hartree
ZPE[B3LYP/6-311++G(d,p)]:	173.607	kcal/mol
U[B3LYP/6-311++G(d,p)]:	13.04	kcal/mol

Table S44. Coordinates and energetics for model serine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**S8**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.905823	0.719186	-0.347093
N2	4.123613	-0.706102	0.593911
C3	4.589408	-0.033764	-0.64932
C4	3.542936	0.860654	-1.2279
O5	3.352064	2.103228	-0.722771
O6	5.925777	1.936958	-0.141045
N7	7.003564	-0.056246	-0.313274
C8	4.586358	-1.9279	0.972362
O9	5.499344	-2.489522	0.368737
C10	3.914673	-2.564723	2.170959
C11	8.309678	0.473244	0.055064
H12	3.380574	-0.262501	1.112332
H13	4.798817	-0.838467	-1.358083
H14	4.230972	2.405035	-0.396825
H15	6.850172	-1.060915	-0.314157
H16	3.449377	-3.499903	1.851308
H17	4.677791	-2.813812	2.910459
H18	3.157189	-1.929898	2.633737
H19	9.075607	-0.240335	-0.247851
H20	8.387223	0.646962	1.133016
H21	8.476646	1.421009	-0.456092
H22	2.670003	0.431519	-1.704381

E[B3LYP/6-311++G(d,p)]:	-570.597419	hartree
E[M05-2X/6-311++G(d,p)]:	-570.513799	hartree
E[M06-2X/6-311++G(d,p)]:	-570.354714	hartree
ZPE[B3LYP/6-311++G(d,p)]:	111.539	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.571	kcal/mol

Table S45. Coordinates and energetics of transition state for hydrogen atom abstraction from C_α of serine model compound by *N*-methylacetamide radical, Structure (**S9**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.050328	-1.119234	-0.329268
N2	3.632952	-0.834001	0.184345
C3	4.845747	-0.175031	-0.18062
C4	5.174436	0.913306	0.842102
O5	5.190618	0.395815	2.167185
O6	6.442775	-1.678938	0.702373
N7	6.660359	-1.223764	-1.511577
C8	2.975446	-1.728721	-0.618703
O9	3.313211	-1.930187	-1.775466
C10	1.808232	-2.45025	0.027576
C11	7.837291	-2.068023	-1.673881
H12	3.341495	-0.726151	1.148017
H13	4.608649	0.492812	-1.327556
H14	6.135464	1.374145	0.581577
H15	5.77152	-0.384243	2.140555
H16	6.254217	-0.800685	-2.348567
H17	1.012947	-2.567372	-0.708926
H18	2.138774	-3.449556	0.325711
H19	1.420869	-1.936042	0.909497
H20	8.226402	-1.925192	-2.681628
H21	7.587589	-3.122785	-1.529288
H22	8.603083	-1.798029	-0.94426
C23	4.327494	1.297335	-2.412345
H24	3.348858	1.718	-2.18511
H25	5.139349	2.018418	-2.348512
C26	4.437387	0.402439	-3.589846
O27	5.52775	-0.074852	-3.925266
N28	3.290621	0.123472	-4.261157
H29	2.424467	0.412797	-3.835659
C30	3.231929	-0.922766	-5.272933
H31	2.34768	-0.770837	-5.894427
H32	4.122297	-0.863619	-5.897778
H33	3.192201	-1.9147	-4.811326
H34	4.405114	1.690076	0.821609

E[B3LYP/6-311++G(d,p)]:	-819.177068	hartree
E[M05-2X/6-311++G(d,p)]:	-819.051178	hartree
E[M06-2X/6-311++G(d,p)]:	-818.821406	hartree
ZPE[B3LYP/6-311++G(d,p)]:	173.577	kcal/mol
U[B3LYP/6-311++G(d,p)]:	12.983	kcal/mol

Table S46. Coordinates and energetics for model serine compound with radical center at C_α, low energy conformation, Structure (**S10**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.375258	0.709243	-0.341622
N2	4.355248	-0.360308	0.926973
C3	5.049153	0.660671	0.297093
C4	4.318004	1.981643	0.275431
O5	3.040577	1.81702	0.905097
O6	6.72735	1.800808	-0.814927
N7	7.159269	-0.392305	-0.397669
C8	4.598497	-1.693774	1.171808
O9	5.613226	-2.293552	0.832248
C10	3.490126	-2.407538	1.918539
C11	8.464351	-0.33539	-1.030017
H12	3.459836	-0.022513	1.268078
H13	4.916765	2.738118	0.796016
H14	2.584052	2.661617	0.924873
H15	6.80748	-1.261312	-0.000803
H16	3.147405	-3.248709	1.311882
H17	3.901884	-2.819392	2.842696
H18	2.63717	-1.771652	2.160885
H19	8.381957	-0.077077	-2.089864
H20	8.935809	-1.313717	-0.936168
H21	9.099289	0.417114	-0.554651
H22	4.204388	2.317102	-0.761533

E[B3LYP/6-311++G(d,p)]:	-570.602639	hartree
E[M05-2X/6-311++G(d,p)]:	-570.515535	hartree
E[M06-2X/6-311++G(d,p)]:	-570.356514	hartree
ZPE[B3LYP/6-311++G(d,p)]:	111.132	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.474	kcal/mol

Table S47. Coordinates and energetics for transition state of N−C_α bond cleavage from model serine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**S11**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.270664	-1.168168	-2.387822
N2	5.163071	0.888492	0.340456
C3	3.933299	-0.732773	-1.962621
C4	3.182648	0.036014	-2.791633
O6	3.569258	0.463627	-3.985747
O7	5.710634	-0.872501	-3.520468
N8	5.983914	-1.912025	-1.514027
C9	4.920566	0.037889	1.40767
O10	5.014504	-1.173773	1.293262
C11	4.621266	0.714889	2.732618
C12	7.347369	-2.326974	-1.801237
H13	4.353673	1.464179	0.092158
H14	3.514002	-1.082533	-1.029867
H19	4.479555	0.068955	-4.125782
H20	5.66308	-1.92557	-0.551534
H21	4.974483	0.075954	3.542141
H22	5.082338	1.701729	2.80449
H23	3.537176	0.833148	2.82827
H24	8.061946	-1.508115	-1.663014
H25	7.414563	-2.664657	-2.834915
H26	7.614004	-3.148486	-1.135558
H27	2.180497	0.358575	-2.523019

E[B3LYP/6-311++G(d,p)]:	-570.565278	hartree
E[M05-2X/6-311++G(d,p)]:	-570.470111	hartree
E[M06-2X/6-311++G(d,p)]:	-570.312262	hartree
ZPE[B3LYP/6-311++G(d,p)]:	108.066	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.163	kcal/mol

Table S48. Coordinates and energetics for *z* ion analogue from N−C_α bond cleavage of model serine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**S12**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.567849	-0.663341	-1.667694
C2	4.195891	-0.358132	-1.267336
C3	3.443791	0.477346	-2.02268
O4	3.847608	1.068992	-3.140584
O5	6.072997	-0.174903	-2.698403
N6	6.279011	-1.513674	-0.878943
C7	7.667553	-1.85057	-1.151811
H8	3.767199	-0.791218	-0.373216
H9	4.785732	0.766912	-3.284777
H10	5.859671	-1.831491	-0.020295
H11	8.353686	-1.074785	-0.796646
H12	7.805966	-1.960965	-2.226757
H13	7.909374	-2.793037	-0.659242
H14	2.422409	0.726861	-1.752226

E[B3LYP/6-311++G(d,p)]:	-361.960889	hartree
E[M05-2X/6-311++G(d,p)]:	-361.903054	hartree
E[M06-2X/6-311++G(d,p)]:	-361.801931	hartree
ZPE[B3LYP/6-311++G(d,p)]:	70.833	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.406	kcal/mol

Table S49. Coordinates and energetics of transition state for C_α–C bond cleavage from model serine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**S13**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.052299	-0.420924	-1.477577
N2	4.655001	0.887874	0.729322
C3	4.191145	0.243672	-0.446491
C4	3.53606	1.003663	-1.383853
O5	3.649756	2.371805	-1.325971
O6	6.339253	0.020685	-2.559142
N7	6.602758	-1.430602	-0.792167
C8	5.173345	0.232323	1.801765
O9	5.34054	-0.986693	1.809967
C10	5.530608	1.089973	2.996876
C11	7.78486	-2.162666	-1.255475
H12	4.597826	1.895378	0.742698
H13	3.902776	-0.789227	-0.310433
H14	3.484008	2.758154	-2.190695
H15	6.24806	-1.586357	0.147714
H16	6.58109	0.926801	3.2457
H17	5.359697	2.15582	2.835624
H18	4.936352	0.75994	3.851817
H19	8.710842	-1.70796	-0.889896
H20	7.800409	-2.157572	-2.345005
H21	7.731541	-3.193376	-0.901417
H22	3.052624	0.566003	-2.245598

E[B3LYP/6-311++G(d,p)]:	-570.555498	hartree
E[M05-2X/6-311++G(d,p)]:	-570.462262	hartree
E[M06-2X/6-311++G(d,p)]:	-570.30447	hartree
ZPE[B3LYP/6-311++G(d,p)]:	109.097	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.177	kcal/mol

Table S50. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of model serine compound with radical center at C_β, C-terminal hydrogen bonding, Structure (**S14**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N1	4.647909	0.875809	0.771425
C2	4.142298	0.231754	-0.360302
C3	3.616466	0.894494	-1.390991
O4	3.543349	2.272668	-1.366144
C5	5.191131	0.198619	1.839842
O6	5.270972	-1.017276	1.868067
C7	5.683796	1.070583	2.978295
H8	4.598877	1.883192	0.794268
H9	4.205896	-0.845417	-0.346631
H10	3.196904	2.600782	-2.199387
H11	6.745772	0.871195	3.13631
H12	5.542953	2.139548	2.805985
H13	5.157159	0.783469	3.890823
H14	3.225394	0.385192	-2.26159

E[B3LYP/6-311++G(d,p)]:	-361.948737	hartree
E[M05-2X/6-311++G(d,p)]:	-361.890255	hartree
E[M06-2X/6-311++G(d,p)]:	-361.790183	hartree
ZPE[B3LYP/6-311++G(d,p)]:	69.916	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.837	kcal/mol

Table S51. Coordinates and energetics for model serine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**S15**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.720815	0.389339	-0.159684
N2	4.858324	-0.596542	1.021944
C3	5.215805	0.062255	-0.246517
C4	4.397175	1.266455	-0.599725
O5	3.083302	1.124225	-0.872141
O6	7.40511	0.013171	0.783733
N7	7.214854	1.086575	-1.204513
C8	3.716448	-1.302749	1.161854
O9	2.82891	-1.293397	0.3007
C10	3.562472	-2.108186	2.431945
C11	8.620507	1.462679	-1.283348
H12	5.626167	-0.691677	1.677638
H13	5.085934	-0.687457	-1.04208
H14	2.812495	0.198744	-0.667376
H15	6.564162	1.417647	-1.901644
H16	2.646516	-1.795592	2.93686
H17	3.446443	-3.160452	2.163273
H18	4.406683	-2.001934	3.114459
H19	8.794257	1.962303	-2.235767
H20	9.256007	0.577297	-1.221788
H21	8.894743	2.13689	-0.468168
H22	4.697347	2.266827	-0.307035

E[B3LYP/6-311++G(d,p)]:	-570.597566	hartree
E[M05-2X/6-311++G(d,p)]:	-570.514184	hartree
E[M06-2X/6-311++G(d,p)]:	-570.355441	hartree
ZPE[B3LYP/6-311++G(d,p)]:	111.135	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.664	kcal/mol

Table S52. Coordinates and energetics for transition state of N−C_α bond cleavage from model serine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**S16**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.723624	-1.153589	-1.809155
N2	5.428417	0.448893	0.557342
C3	4.594692	-0.445564	-1.138724
C4	4.00555	0.641246	-1.810383
O6	3.069172	1.352923	-1.286957
O7	6.323662	-0.68032	-2.766773
N8	6.034179	-2.370062	-1.275419
C9	4.56164	0.939259	1.412767
O10	3.333959	1.113769	1.118775
C11	4.988038	1.325988	2.814559
C12	7.134859	-3.172344	-1.786909
H13	6.39559	0.35639	0.844211
H14	3.969883	-1.004035	-0.452522
H19	3.079098	1.204507	-0.186671
H20	5.553403	-2.672782	-0.443709
H21	4.363748	0.787542	3.531399
H22	6.038216	1.110169	3.014724
H23	4.804262	2.393236	2.956627
H24	7.110856	-3.172795	-2.876887
H25	7.027264	-4.194869	-1.42437
H26	8.106277	-2.779909	-1.469435
H27	4.375796	0.935747	-2.789687

E[B3LYP/6-311++G(d,p)]:	-570.564791	hartree
E[M05-2X/6-311++G(d,p)]:	-570.473248	hartree
E[M06-2X/6-311++G(d,p)]:	-570.31319	hartree
ZPE[B3LYP/6-311++G(d,p)]:	107.584	kcal/mol
U[B3LYP/6-311++G(d,p)]:	8.69	kcal/mol

Table S53. Coordinates and energetics for *z* ion analogue from N−C_α bond cleavage of model serine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**S17**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.630132	-1.357391	-2.133768
C2	4.40119	-0.704311	-1.649469
C3	3.930041	0.528445	-2.220202
O4	2.905076	1.080541	-1.822209
O5	6.311361	-0.888183	-3.041587
N6	5.957048	-2.523445	-1.500912
C7	7.14607	-3.276047	-1.870299
H8	3.813174	-1.135649	-0.844713
H9	5.370479	-2.863052	-0.755987
H10	7.112699	-3.553024	-2.926524
H11	7.193842	-4.178711	-1.26225
H12	8.048702	-2.681962	-1.706406
H13	4.53466	0.955072	-3.034676

E[B3LYP/6-311++G(d,p)]:	-361.302941	hartree
E[M05-2X/6-311++G(d,p)]:	-361.24156	hartree
E[M06-2X/6-311++G(d,p)]:	-361.142302	hartree
ZPE[B3LYP/6-311++G(d,p)]:	61.453	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.814	kcal/mol

Table S54. Coordinates and energetics of transition state for C_α–C bond cleavage from model serine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**S18**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	6.445125	-1.25273	-0.835096
N2	5.339977	0.861367	0.526087
C3	4.602204	0.034262	-0.369512
C4	4.148161	0.538706	-1.551969
O5	3.270629	-0.118336	-2.367325
O6	7.423651	-1.041732	-0.159551
N7	6.333446	-1.977185	-1.954488
C8	4.708355	1.577326	1.517091
O9	3.495859	1.680159	1.587703
C10	5.636132	2.250322	2.512888
C11	7.458873	-2.645269	-2.618589
H12	6.318462	0.624528	0.650789
H13	4.06638	-0.805295	0.074927
H14	2.754922	-0.748081	-1.848293
H15	5.445452	-1.938512	-2.431246
H16	5.414075	1.866932	3.511155
H17	6.694692	2.09616	2.296077
H18	5.422985	3.320956	2.518011
H19	7.79144	-2.083116	-3.495729
H20	7.166991	-3.651479	-2.924714
H21	8.281767	-2.712655	-1.908936
H22	4.536125	1.445794	-1.995379

E[B3LYP/6-311++G(d,p)]:	-570.547724	hartree
E[M05-2X/6-311++G(d,p)]:	-570.4544	hartree
E[M06-2X/6-311++G(d,p)]:	-570.296595	hartree
ZPE[B3LYP/6-311++G(d,p)]:	108.895	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.303	kcal/mol

Table S55. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of model serine compound with radical center at C_β, N-terminal hydrogen bonding, Structure (**S19**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N1	4.891504	1.133806	0.520141
C2	3.971829	0.567575	-0.379109
C3	4.311689	0.066709	-1.568234
O4	3.453934	-0.494741	-2.474928
C5	4.515305	1.638903	1.742456
O6	3.356315	1.62711	2.122874
C7	5.639967	2.207499	2.585462
H8	5.86472	1.172213	0.260154
H9	2.954001	0.574754	-0.00804
H10	2.553937	-0.481778	-2.129366
H11	5.69042	1.649742	3.52305
H12	6.617066	2.172992	2.098713
H13	5.401352	3.243724	2.832927
H14	5.329375	0.057685	-1.941226

E[B3LYP/6-311++G(d,p)]:	-361.943071	hartree
E[M05-2X/6-311++G(d,p)]:	-361.883976	hartree
E[M06-2X/6-311++G(d,p)]:	-361.784201	hartree
ZPE[B3LYP/6-311++G(d,p)]:	69.872	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.763	kcal/mol

Table S56. Coordinates and energetics for transition state of N−C_α bond cleavage from model O-methyl threonine compound with radical center at C_β, Structure (**S20**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.059406	0.775605	-2.255503
N2	6.539888	1.898803	-0.073236
C3	5.524261	0.121822	-0.985859
C4	4.725809	-0.3237	0.044056
C5	3.313061	0.095113	0.304451
O6	5.329241	-1.158331	0.907238
O7	5.66379	1.710208	-2.770296
N8	3.943748	0.240489	-2.832184
C9	5.904557	2.553581	0.928462
O10	5.264671	2.001463	1.825789
C11	6.095298	4.074916	0.938283
C12	3.435427	0.720494	-4.109372
H13	6.610744	2.410302	-0.952797
H14	6.526719	-0.283424	-1.028878
H16	2.649498	-0.774551	0.375709
H17	3.262989	0.646093	1.24668
H18	2.949894	0.749096	-0.485296
H20	3.594418	-0.633165	-2.471932
H21	5.700722	4.472873	1.872558
H22	7.148689	4.346012	0.837993
H23	5.554062	4.519094	0.09722
H24	2.36772	0.505002	-4.177229
H25	3.951416	0.254841	-4.955148
H26	3.590925	1.796792	-4.168508
C26	4.872595	-1.239746	2.267071
H27	5.554764	-1.933725	2.75389
H28	4.937329	-0.252773	2.728662
H29	3.854283	-1.633354	2.322773

E[B3LYP/6-311++G(d,p)]:	-649.181263	hartree
E[M05-2X/6-311++G(d,p)]:	-649.072997	hartree
E[M06-2X/6-311++G(d,p)]:	-648.889101	hartree
ZPE[B3LYP/6-311++G(d,p)]:	143.672	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.684	kcal/mol

Table S57. Coordinates and energetics for *c* ion analogue from N−C_α bond cleavage of model O-methyl threonine compound with radical center at C_β, Structure (**S21**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	5.967103	1.680314	-0.632175
C9	5.698944	2.113194	0.639192
O10	5.596788	1.264218	1.527469
C11	5.729029	3.592464	0.898518
H13	5.513066	0.776874	-0.79871
H21	5.310719	3.807548	1.881107
H22	6.765237	3.940713	0.864118
H23	5.175507	4.128453	0.123886

E[B3LYP/6-311++G(d,p)]:	-208.601605	hartree
E[M05-2X/6-311++G(d,p)]:	-208.557576	hartree
E[M06-2X/6-311++G(d,p)]:	-208.499509	hartree
ZPE[B3LYP/6-311++G(d,p)]:	36.938	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.02	kcal/mol

Table S58. Coordinates and energetics for *c* ion analogue from N−C_α bond cleavage of model O-methyl threonine compound with radical center at C_β, Structure (**S22**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.941604	0.047843	-2.601256
C3	5.352461	-0.676196	-1.370095
C4	4.600715	-1.023108	-0.310768
C5	3.141345	-0.730114	-0.104322
O6	5.243071	-1.735979	0.671547
O7	5.623535	0.954714	-3.061993
N8	3.775006	-0.35425	-3.208099
C12	3.363106	0.222958	-4.480559
H14	6.418795	-0.860704	-1.304937
H16	2.566803	-1.656094	0.011253
H17	2.985342	-0.136514	0.800996
H18	2.738401	-0.168609	-0.943758
H20	3.421222	-1.266908	-2.967646
H24	2.341333	-0.091781	-4.698049
H25	4.017771	-0.083112	-5.303761
H26	3.395599	1.310397	-4.414531
C26	4.838406	-1.581638	2.03054
H27	5.519068	-2.203519	2.609904
H28	4.937091	-0.541282	2.35878
H29	3.813488	-1.925297	2.197866

E[B3LYP/6-311++G(d,p)]:	-440.575011	hartree
E[M05-2X/6-311++G(d,p)]:	-440.50191	hartree
E[M06-2X/6-311++G(d,p)]:	-440.376201	hartree
ZPE[B3LYP/6-311++G(d,p)]:	105.179	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.916	kcal/mol

Table S59. Coordinates and energetics of transition state for C_α–C bond cleavage from model O-methyl threonine compound with radical center at C_β, Structure (**S23**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.949928	0.996223	-2.775868
N2	5.728633	2.198047	-0.390193
C3	5.55379	0.795275	-0.560026
C4	4.556165	0.104788	0.067277
C5	3.380999	0.697461	0.771852
O6	4.57094	-1.257452	-0.158831
O7	5.114658	2.044277	-3.352922
N8	4.36236	-0.131313	-3.188314
C9	6.086175	2.791971	0.795498
O10	6.168448	2.187273	1.851769
C11	6.362187	4.284334	0.704343
C12	3.775199	-0.323473	-4.518483
H13	5.743896	2.752727	-1.237957
H14	6.421244	0.226357	-0.880715
H16	2.443406	0.279264	0.386522
H17	3.416889	0.514435	1.850734
H18	3.367883	1.777192	0.62727
H20	4.30603	-0.878717	-2.509606
H21	7.397025	4.465044	1.004891
H22	6.201624	4.700095	-0.292366
H23	5.719421	4.803365	1.418334
H24	2.704804	-0.53257	-4.443483
H25	4.265317	-1.14885	-5.040836
H26	3.918696	0.592893	-5.089104
C26	4.25214	-2.106358	0.94727
H27	4.371928	-3.127897	0.588193
H28	4.939653	-1.926964	1.779605
H29	3.221477	-1.96174	1.2839

E[B3LYP/6-311++G(d,p)]:	-649.189551	hartree
E[M05-2X/6-311++G(d,p)]:	-649.082505	hartree
E[M06-2X/6-311++G(d,p)]:	-648.899019	hartree
ZPE[B3LYP/6-311++G(d,p)]:	143.831	kcal/mol
U[B3LYP/6-311++G(d,p)]:	10.58	kcal/mol

Table S60. Coordinates and energetics of *a* ion analogue from C_α−C bond cleavage of model O-methyl threonine compound with radical center at C_β, Structure (**S24**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
N2	5.849805	2.147028	-0.383194
C3	5.63886	0.750878	-0.516221
C4	4.588204	0.094711	-0.009036
C5	3.440505	0.714042	0.727446
O6	4.536486	-1.258898	-0.255778
C9	5.985234	2.816444	0.815005
O10	5.800195	2.292967	1.898701
C11	6.371122	4.281271	0.688799
H13	6.130504	2.647059	-1.213573
H14	6.397823	0.197646	-1.058778
H16	2.501388	0.246736	0.416052
H17	3.546234	0.6094	1.810915
H18	3.38992	1.781438	0.514014
H21	7.312124	4.438073	1.220474
H22	6.481687	4.624582	-0.342143
H23	5.610784	4.887799	1.184754
C26	4.280441	-2.099645	0.869239
H27	4.305117	-3.121696	0.492983
H28	5.05408	-1.97295	1.634691
H29	3.297719	-1.904427	1.309663

E[B3LYP/6-311++G(d,p)]:	-440.576535	hartree
E[M05-2X/6-311++G(d,p)]:	-440.504706	hartree
E[M06-2X/6-311++G(d,p)]:	-440.379529	hartree
ZPE[B3LYP/6-311++G(d,p)]:	104.772	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.917	kcal/mol

Table S61. Coordinates and energetics of *x* ion analogue from C_α–C bond cleavage of model O-methyl threonine compound with radical center at C_β, Structure (**S25**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.04886	1.005273	-2.974598
O7	5.219359	2.025069	-3.57891
N8	4.361268	-0.093913	-3.308224
C12	3.67323	-0.281323	-4.593335
H20	4.371332	-0.855435	-2.649045
H24	2.667707	-0.671291	-4.425163
H25	4.225016	-0.968526	-5.240038
H26	3.60204	0.687476	-5.084743

E[B3LYP/6-311++G(d,p)]:	-208.614729	hartree
E[M05-2X/6-311++G(d,p)]:	-208.573389	hartree
E[M06-2X/6-311++G(d,p)]:	-208.516261	hartree
ZPE[B3LYP/6-311++G(d,p)]:	38.664	kcal/mol
U[B3LYP/6-311++G(d,p)]:	3.133	kcal/mol

Table S62. Coordinates and energetics of transition state for loss of isocyanic acid from terminal nitrogen-centered radical, Structure (**S26**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-2.080618	-1.80886	2.008827
C2	-1.834954	-0.653685	1.065614
O3	-2.73578	-0.012507	0.552544
N4	-0.508727	-0.36746	0.798905
C5	-0.120363	0.62652	-0.134983
C6	-0.08928	-0.178917	-1.704886
O7	0.98373	-0.674757	-1.956819
C8	1.259116	1.201638	0.106019
H11	-1.209011	-2.060237	2.616404
H12	-2.919322	-1.558531	2.658557
H13	-2.365062	-2.687186	1.421669
H14	0.199651	-1.011179	1.124224
H15	-0.896927	1.382041	-0.192513
H16	1.512032	1.917395	-0.677001
H17	1.267858	1.722766	1.068879
H18	2.020778	0.420465	0.102829
N17	-1.242485	-0.006631	-2.254379
H19	-2.047885	0.166291	-1.657817

E[B3LYP/6-311++G(d,p)]:	-455.997226	hartree
E[M05-2X/6-311++G(d,p)]:	-455.919204	hartree
E[M06-2X/6-311++G(d,p)]:	-455.792045	hartree
ZPE[B3LYP/6-311++G(d,p)]:	88.711	kcal/mol
U[B3LYP/6-311++G(d,p)]:	6.403	kcal/mol

Table S63. Coordinates and energetics of *a* ion analogue from loss of isocyanic acid from terminal nitrogen-centered radical, Structure (**S27**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	-2.234605	-1.340148	4.038695
C2	-2.218827	0.003016	3.335686
O3	-3.208991	0.709689	3.243685
N4	-1.001025	0.383421	2.799073
C5	-0.79224	1.562595	2.107212
C8	0.579413	1.927831	1.663756
H11	-1.264616	-1.842887	4.049862
H12	-2.570383	-1.19568	5.068103
H13	-2.963117	-1.988218	3.545621
H14	-0.220709	-0.247779	2.910436
H15	-1.647696	2.216437	2.041314
H16	0.542381	2.788473	0.994108
H17	1.238884	2.197619	2.504313
H18	1.07246	1.108894	1.122916

E[B3LYP/6-311++G(d,p)]:	-287.277923	hartree
E[M05-2X/6-311++G(d,p)]:	-287.221176	hartree
E[M06-2X/6-311++G(d,p)]:	-287.135902	hartree
ZPE[B3LYP/6-311++G(d,p)]:	72.483	kcal/mol
U[B3LYP/6-311++G(d,p)]:	5.012	kcal/mol

Table S64. Coordinates and energetics of isocyanic acid, Structure (**S28**)

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C6	0.681078	-1.196123	-4.971524
O7	0.765452	-2.149268	-4.305975
N17	0.614303	-0.123699	-5.532397
H19	0.452445	0.020107	-6.515397

E[B3LYP/6-311++G(d,p)]:	-168.738762	hartree
E[M05-2X/6-311++G(d,p)]:	-168.70959	hartree
E[M06-2X/6-311++G(d,p)]:	-168.668231	hartree
ZPE[B3LYP/6-311++G(d,p)]:	13.339	kcal/mol
U[B3LYP/6-311++G(d,p)]:	2.039	kcal/mol

Table S65. Coordinates and energetics of noncovalent interaction of products following N−C_α bond cleavage of valine model compound with radical center at C_β, structure not shown

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	7.097674	0.36544	-0.222861
N2	3.897586	1.716798	-2.573356
C3	5.874788	-0.473237	-0.404332
C4	5.791078	-1.673253	-1.008501
C5	4.468452	-2.397192	-1.063748
O7	8.250767	-0.026462	-0.385202
N8	6.82185	1.642429	0.177591
C9	3.213682	2.270082	-1.521188
O10	3.831444	2.504382	-0.479945
C11	1.799172	2.710677	-1.765316
C12	7.884127	2.612752	0.383309
H13	4.545299	0.98262	-2.260502
H14	4.969003	-0.061252	0.034834
H16	3.664839	-1.831025	-0.588223
H17	4.181802	-2.609753	-2.10051
H18	4.546201	-3.367901	-0.560408
H20	5.863657	1.967092	0.160758
H21	1.2342	1.926637	-2.275762
H22	1.323046	2.969125	-0.820245
H23	1.806984	3.586883	-2.420054
H24	7.486679	3.461003	0.942206
H25	8.30057	2.972681	-0.564057
H26	8.693953	2.152524	0.950539
C25	6.937477	-2.401235	-1.655337
H27	7.857467	-1.823862	-1.631023
H28	7.10853	-3.351428	-1.134979
H29	6.679775	-2.657361	-2.690175

E[B3LYP/6-311++G(d,p)]:	-573.96075	hartree
E[M05-2X/6-311++G(d,p)]:	-573.855109	hartree
E[M06-2X/6-311++G(d,p)]:	-573.686918	hartree
ZPE[B3LYP/6-311++G(d,p)]:	139.711	kcal/mol
U[B3LYP/6-311++G(d,p)]:	10.596	kcal/mol

Table S66. Coordinates and energetics of noncovalent interaction of products following N−C_α bond cleavage of threonine model compound with radical center at C_β, structure not shown

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	5.264445	-1.177516	-2.46403
N2	5.093693	1.26718	0.695445
C3	3.941073	-0.745902	-2.007841
C4	3.091245	-0.108888	-2.864217
C5	1.70899	0.332834	-2.497087
O6	3.42071	0.172188	-4.123028
O7	5.637691	-0.995265	-3.644768
N8	6.064282	-1.793856	-1.559955
C9	4.931599	0.277754	1.631914
O10	5.208243	-0.881686	1.317398
C11	4.581804	0.698045	3.030892
C12	7.414281	-2.222525	-1.894206
H13	4.746053	0.982301	-0.230007
H14	3.60188	-1.009763	-1.014767
H16	0.980559	-0.168618	-3.141105
H17	1.477907	0.106799	-1.455781
H18	1.602716	1.408569	-2.667077
H19	4.341297	-0.205517	-4.256613
H20	5.793789	-1.754281	-0.58499
H21	4.320568	-0.177467	3.624262
H22	5.443775	1.199518	3.480295
H23	3.755135	1.413264	3.023422
H24	8.128862	-1.392384	-1.863588
H25	7.421466	-2.639321	-2.900886
H26	7.728887	-2.988209	-1.183807

E[B3LYP/6-311++G(d,p)]:	-609.904484	hartree
E[M05-2X/6-311++G(d,p)]:	-609.800092	hartree
E[M06-2X/6-311++G(d,p)]:	-609.627447	hartree
ZPE[B3LYP/6-311++G(d,p)]:	125.786	kcal/mol
U[B3LYP/6-311++G(d,p)]:	9.875	kcal/mol

Table S67. Coordinates and energetics of noncovalent interaction of products following N−C_α bond cleavage of O-methyl threonine model compound with radical center at C_β, structure not shown.

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
C1	4.519149	-0.847164	-2.781309
N2	6.485272	1.370138	-0.726519
C3	4.880327	-1.766188	-1.676682
C4	4.152104	-2.000576	-0.57155
C5	2.80546	-1.418905	-0.255166
O6	4.707612	-2.838899	0.35181
O7	5.218522	0.136994	-3.049349
N8	3.396481	-1.125877	-3.495111
C9	5.523018	1.823547	0.145395
O10	4.859429	1.042472	0.81704
C11	5.445138	3.325984	0.309143
C12	2.972401	-0.306499	-4.622146
H13	6.103217	0.894658	-1.569588
H14	5.901352	-2.130958	-1.697381
H16	2.092094	-2.206026	0.010109
H17	2.885328	-0.727093	0.587362
H18	2.41236	-0.861805	-1.103019
H20	2.96952	-2.02807	-3.357131
H21	4.517922	3.583283	0.821425
H22	6.295673	3.663779	0.90825
H23	5.499832	3.832147	-0.658012
H24	1.938935	-0.551425	-4.87111
H25	3.602592	-0.470147	-5.501709
H26	3.038075	0.747491	-4.351311
C26	4.472889	-2.58117	1.741206
H27	5.102824	-3.289916	2.276642
H28	4.763172	-1.559711	2.000214
H29	3.428287	-2.755827	2.015713

E[B3LYP/6-311++G(d,p)]:	-649.188325	hartree
E[M05-2X/6-311++G(d,p)]:	-649.078112	hartree
E[M06-2X/6-311++G(d,p)]:	-648.894228	hartree
ZPE[B3LYP/6-311++G(d,p)]:	142.792	kcal/mol
U[B3LYP/6-311++G(d,p)]:	11.09	kcal/mol

Table S68. Coordinates and energetics of water, structure not labeled

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
O6	-0.061471	-0.022629	0
H13	0.223984	0.896123	0
H27	0.751601	-0.536978	0
E[B3LYP/6-311++G(d,p)]:		-76.458532	hartree
E[M05-2X/6-311++G(d,p)]:		-76.441479	hartree
E[M06-2X/6-311++G(d,p)]:		-76.420943	hartree
ZPE[B3LYP/6-311++G(d,p)]:		13.355	kcal/mol
U[B3LYP/6-311++G(d,p)]:		1.779	kcal/mol

Table S69. Coordinates and energetics of methanol, structure not labeled

Atom Label	X coord [A]	Y coord [A]	Z coord [A]
O6	5.129876	2.315981	-2.005757
H13	4.273011	1.885267	-1.938985
C26	4.940141	3.726176	-1.95962
H27	5.929427	4.177952	-2.036039
H28	4.328647	4.088548	-2.795234
H29	4.483103	4.051126	-1.016765
E[B3LYP/6-311++G(d,p)]:		-115.764998	hartree
E[M05-2X/6-311++G(d,p)]:		-115.737365	hartree
E[M06-2X/6-311++G(d,p)]:		-115.704326	hartree
ZPE[B3LYP/6-311++G(d,p)]:		32.023	kcal/mol
U[B3LYP/6-311++G(d,p)]:		2.105	kcal/mol

References

1. Lee, M.; Kang, M.; Moon, B.; Oh, H. B. Gas-phase Peptide Sequencing by TEMPO-mediated Radical Generation. *Analyst* **2009,** *134* (8), 1706-1712.
2. Sohn, C. H. New Reagents and Methods for Mass Spectrometry-based Proteomics Investigations. Ph.D. Dissertation, California Institute of Technology, Pasadena, CA, 2011.
3. Sun, Q.; Nelson, H.; Ly, T.; Stoltz, B. M.; Julian, R. R. Side Chain Chemistry Mediates Backbone Fragmentation in Hydrogen Deficient Peptide Radicals. *J. Proteome Res.* **2008,** *8* (2), 958-966.
4. Moore, B. N.; Julian, R. R. Dissociation Energies of X-H Bonds in Amino Acids. *Phys. Chem. Chem. Phys.* **2012,** *14* (9), 3148-3154.
5. Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003,** *36* (4), 255-263.
6. Wyttenbach, T.; von Helden, G.; Bowers, M. T. Gas-Phase Conformation of Biological Molecules: Bradykinin. *J. Am. Chem. Soc.* **1996,** *118* (35), 8355-8364.
7. Tao, L.; McLean, J.; McLean, J.; Russell, D. A Collision Cross-section Database of Singly-Charged Peptide Ions. *J. Am. Soc. Mass Spectrom.* **2007,** *18* (7), 1232-1238.
8. Hodyss, R.; Cox, H. A.; Beauchamp, J. L. Bioconjugates for Tunable Peptide Fragmentation: Free Radical Initiated Peptide Sequencing (FRIPS). *J. Am. Chem. Soc.* **2005,** *127* (36), 12436-12437.
9. Moore, B.; Sun, Q.; Hsu, J.; Lee, A.; Yoo, G.; Ly, T.; Julian, R. Dissociation Chemistry of Hydrogen-Deficient Radical Peptide Anions. *J. Am. Soc. Mass Spectrom.* **2012,** *23* (3), 460-468.
10. Yu, W.; Vath, J. E.; Huberty, M. C.; Martin, S. A. Identification of the Facile Gas-phase Cleavage of the Asp-Pro and Asp-Xxx Peptide Bonds in Matrix-Assisted Laser Desorption Time-of-Flight Mass Spectrometry. *Anal. Chem.* **1993,** *65* (21), 3015-3023.
11. Lee, S.-W.; Kim, H. S.; Beauchamp, J. L. Salt Bridge Chemistry Applied to Gas-Phase Peptide Sequencing: Selective Fragmentation of Sodiated Gas-Phase Peptide Ions Adjacent to Aspartic Acid Residues. *J. Am. Chem. Soc.* **1998,** *120* (13), 3188-3195.
12. Tsaprailis, G.; Nair, H.; Somogyi, Á.; Wysocki, V. H.; Zhong, W.; Futrell, J. H.; Summerfield, S. G.; Gaskell, S. J. Influence of Secondary Structure on the Fragmentation of Protonated Peptides. *J. Am. Chem. Soc.* **1999,** *121* (22), 5142-5154.
13. Gu, C.; Tsaprailis, G.; Breci, L.; Wysocki, V. H. Selective Gas-Phase Cleavage at the Peptide Bond C-Terminal to Aspartic Acid in Fixed-Charge Derivatives of Asp-Containing Peptides. *Anal. Chem.* **2000,** *72* (23), 5804-5813.
14. Xia, Y.; Chrisman, P. A.; Pitteri, S. J.; Erickson, D. E.; McLuckey, S. A. Ion/Molecule Reactions of Cation Radicals Formed from Protonated Polypeptides via Gas-Phase Ion/Ion Electron Transfer. *J. Am. Chem. Soc.* **2006,** *128* (36), 11792-11798.
15. Moore, B. N.; Blanksby, S. J.; Julian, R. R. Ion-Molecule Reactions Reveal Facile Radical Migration in Peptides. *Chem. Commun.* **2009,** (33), 5015-5017.